

Final Technical  
Progress Report

June 2000–  
May 2003

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# **CO<sub>2</sub> Acquisition Membrane (CAM) Project**



**MCR-00-509**

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**Final  
Technical Progress Report**

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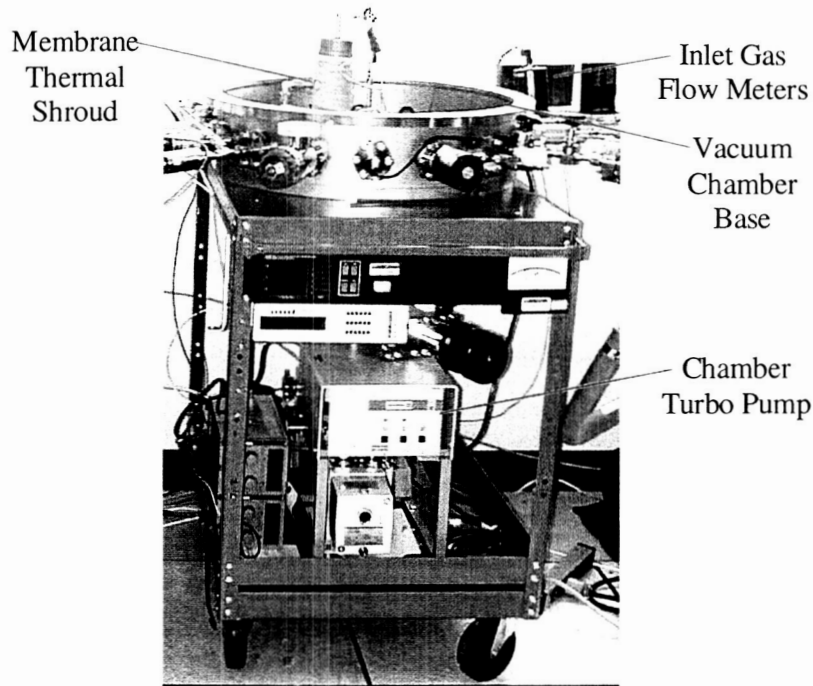
## Introduction

The CO<sub>2</sub> Acquisition Membrane (CAM) project was performed to develop, test, and analyze thin film membrane materials for separation and purification of carbon dioxide (CO<sub>2</sub>) from mixtures of gases, such as those found in the Martian atmosphere. The membranes developed in this project are targeted toward *In Situ Resource Utilization (ISRU)* applications, such as *In Situ Propellant Production (ISPP)* and *In Situ Consumables Production (ISCP)*. These membrane materials may be used in a variety of ISRU systems, for example as the atmospheric inlet filter for an ISPP process to enhance the concentration of CO<sub>2</sub> for use as a reactant gas, to passively separate argon and nitrogen trace gases from CO<sub>2</sub> for habitat pressurization, to provide a system for removal of CO<sub>2</sub> from breathing gases in a closed environment, or within a process stream to selectively separate CO<sub>2</sub> from other gaseous components. The membranes identified and developed for CAM were evaluated for use in candidate ISRU processes and other gas separation applications, and will help to lay the foundation for future unmanned sample return and human space missions.

CAM is a cooperative project split among three institutions: Lockheed Martin Astronautics (LMA) to develop the , the Colorado School of Mines (CSM), and Marshall Space Flight Center (MSFC).

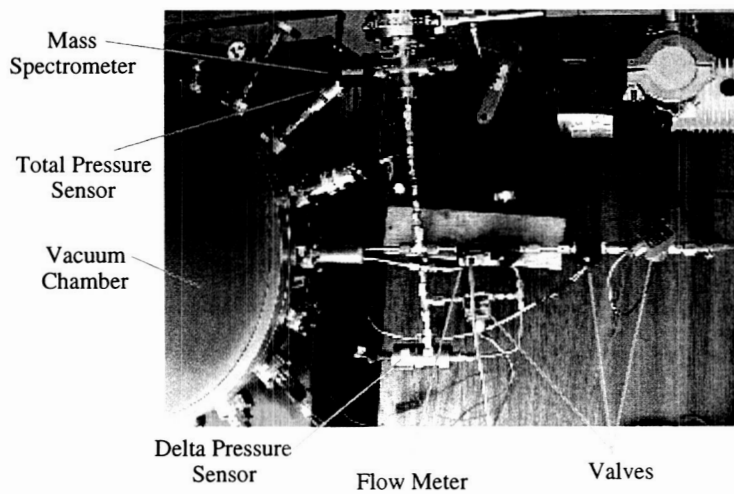
## The Membrane Test Facility at Lockheed Martin

The Membrane Test Facility (MTF) was developed to measure the gas permeation characteristics of membranes using pure gas and simulated Mars atmosphere environments. The experiments were performed over a range of temperature and pressure conditions including those found on Mars. Figure 1 shows a photograph of the MTF in the Spacecraft Technology Development Laboratory at Lockheed Martin. The membrane under test is located inside the thermal shroud.



*Figure 1 Membrane Test Facility*

Figure 2 shows a top view of the instrumentation outside the MTF vacuum chamber that measures the gas that permeates through the membrane.



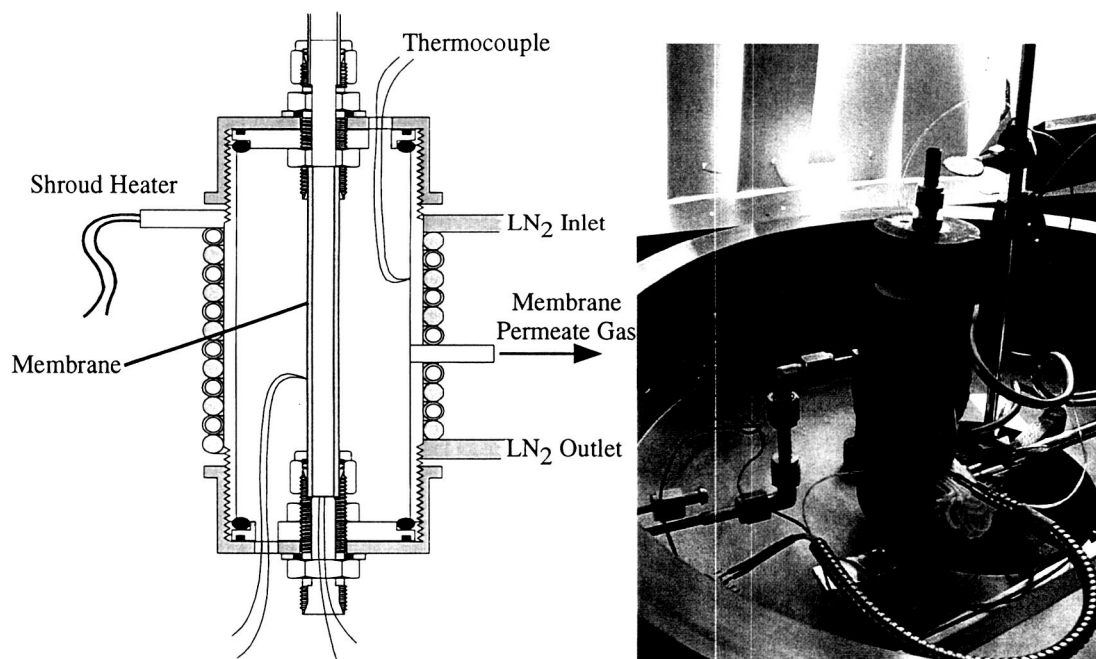
*Figure 2 MTF Gas Measurement Instrumentation*

The MTF consists of an instrumented vacuum chamber that includes capability for closed loop control of chamber pressure, trans-membrane (delta) pressure, temperature, and chamber gas composition. The MTF is a two volume compartment system that is used to

measure separation of gases through a membrane positioned between the compartments. The much larger chamber compartment contains a known composition of gases for the experiments. The smaller membrane permeate compartment is where the gases that pass through the membrane are measured for pressure, flow rate, and composition. A series of valves under computer control allow manipulation of chamber gases and access to the chamber and membrane permeate compartments. Two mass spectrometers are used in the MTF, one in each compartment to control the chamber gas composition and measure the composition of the gases that permeate through the membrane.

### MTF Thermal Shroud

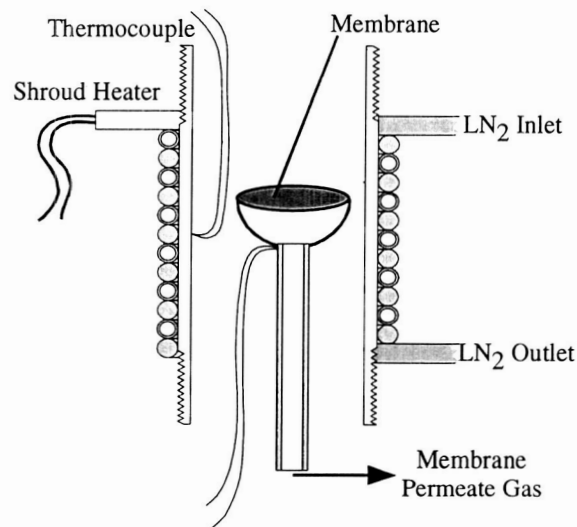
The MTF thermal shroud assembly is shown in Figure 3. The thermal shroud was designed to support the membrane under test within the vacuum chamber, and surround it with a controlled thermal and gaseous environment. The shroud provides the mechanical and thermal interface to membrane. The membrane element can have either a cylindrical ceramic or a planar sheet geometry. The cylindrical membrane is shown in the schematic, where the central cylinder represents the membrane, and the outer surface the shroud. The membrane is located on the inner surface of the ceramic support, and gas permeates from the center of the support outward into the annular space within the shroud. A tube fitting is mounted in the side of the shroud to provide access to the membrane permeate gas compartment that is present within the annular space. End caps on the shroud provide a seal between the chamber and membrane gas compartments. The membrane support tube passes through the end caps to allow the chamber gas to access the membrane surface.



*Figure 3 (left) Thermal Shroud Assembly Schematic Diagram  
(right) Photograph of Thermal Shroud*



An alternate shroud configuration is used for planar membranes. This configuration uses a commercial stainless steel membrane holder to support the membrane that is positioned in the center of the shroud with the end caps removed to allow chamber gas to access the membrane surface. Silver coated copper braid is used to facilitate conductive heat transfer between the thermal shroud and membrane holder. Figure 4 shows a schematic of the planar membrane holder within the thermal shroud.



*Figure 4 Alternate Configuration for Planar Membrane Holder in Thermal Shroud*

The shroud assembly provides thermal control of the membranes during experiments. The outside of the shroud is wound with both copper tubing and an electrical heater to allow both heating and cooling to be applied. A copper coating was plasma sprayed on the outside of the shroud to provide mechanical support and thermal contact between the heater, copper tube, and shroud. Thermal control of the membrane is accomplished through heat transfer between the shroud and the membrane. Convective heat transfer occurs at a level determined by the total pressure of the chamber. Shroud cooling is accomplished by flowing liquid nitrogen through the copper tubing under control of a solenoid and metering valve. Heating is accomplished by applying electrical power to the heater coil. The shroud was sized to be as small as possible to interface with membranes of the planned size, and minimize the time associated with temperatures transients during experiments.

#### Development of MTF Software for Control and Data Acquisition

Software was developed to control various parameters within the MTF during experiments, and to acquire data during membrane gas permeation experiments. The software was developed in modules that utilize a graphical user interface for control and data display capabilities. Figure 5 shows a status screen that depicts a virtual representation of the MTF and displays the current status of parameters that are measured

during the course of membrane evaluation experiments. The solenoid valves, flow controls, and chamber fan may be manually actuated using the controls shown on the diagram.

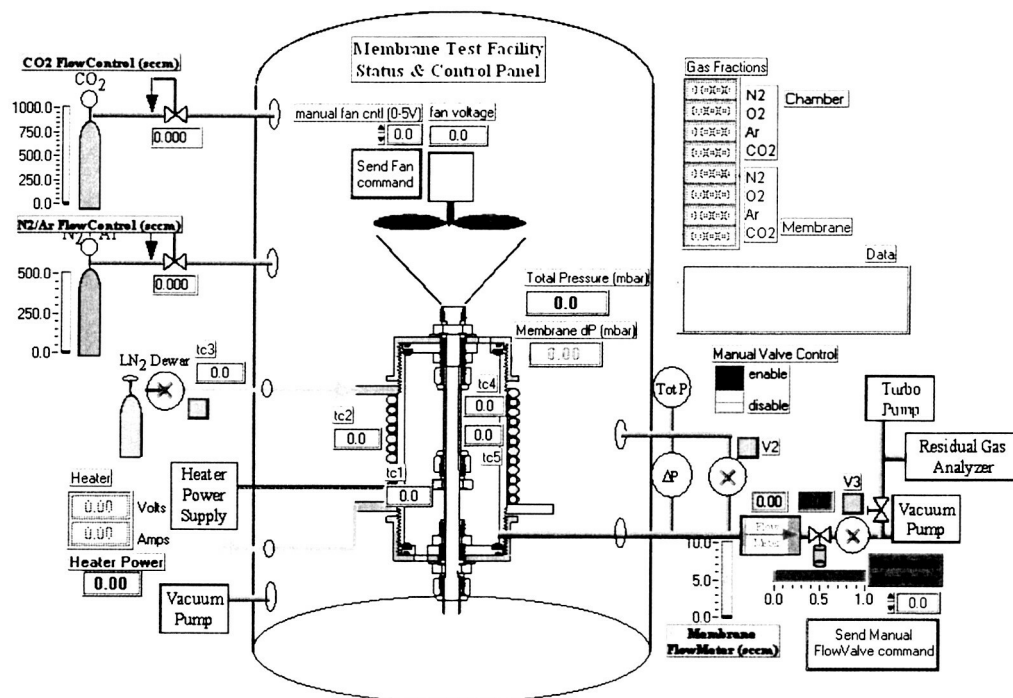


Figure 5 Membrane Test Facility Virtual Schematic and Status Screen

Gas composition is measured with two separate mass spectrometers that sample gas from the MTF chamber and membrane permeate gas compartments. The membrane permeate gas flow rate is measured using a sensitive flow meter that is connected to a proportional valve and a dedicated vacuum pump. The proportional valve controls the delta pressure across the membrane, and is measured using a differential pressure gauge that is connected between the two gas compartments.

The data display capabilities of the MTF software are shown in Figure 6, the main control panel. Set points for the various control loops are set on this panel, and data are graphically displayed. Experimental data is acquired at user defined time intervals, and continuously written to data files for post processing and analysis.

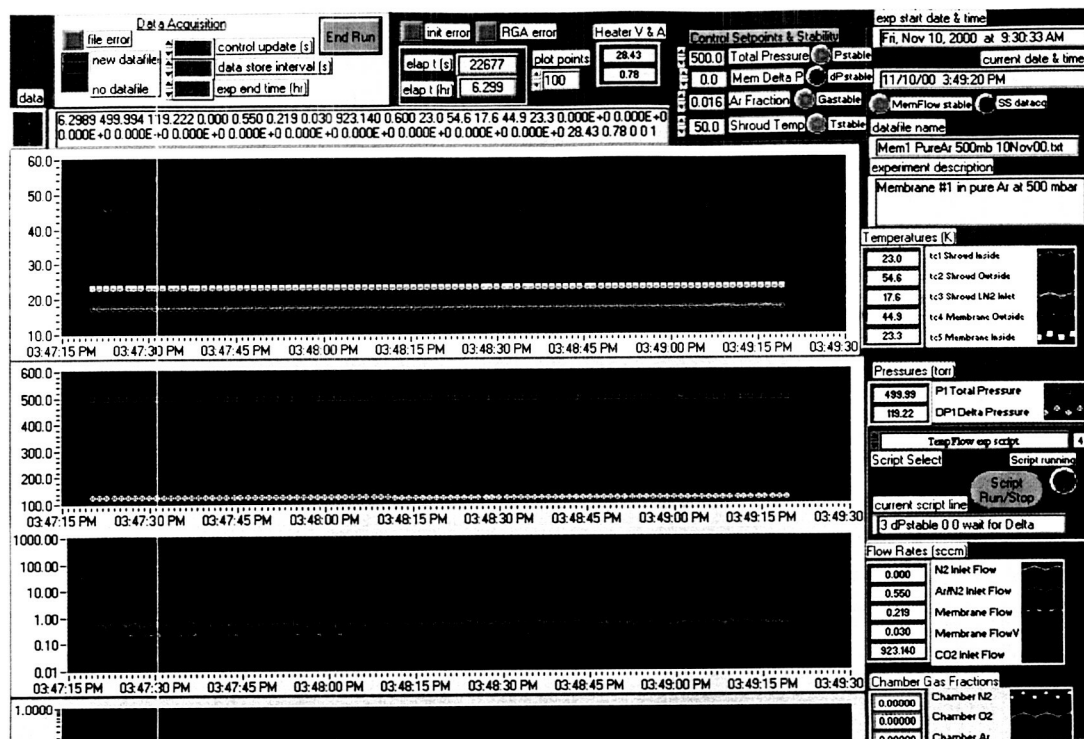


Figure 6 Membrane Test Facility Main User Interface Panel

The software includes capabilities for closed loop control of chamber total pressure, chamber gas composition, and membrane temperature. The control software was developed using a Proportional Integral Differential (PID) algorithm to generate the signal appropriate for control of the system. Capabilities were also included to disable the automatic control, and allow the user to manually command the control outputs.

The intent of the CAM experiments is to measure the gas separation capabilities of candidate membranes on gas mixtures that simulate the Martian atmosphere. The pressure and composition of Mars atmospheric gases were measured by the Viking spacecraft, and are shown in Table 1. These data provide control loop set points for the chamber gas compositions used in CAM experiments.

Table 1 Martian Atmosphere Gas Composition

| Parameter                    | Value  |
|------------------------------|--------|
| Total Pressure               | 6 mbar |
| CO <sub>2</sub> Gas Fraction | 0.95   |
| Ar Gas Fraction              | 0.024  |
| N <sub>2</sub> Gas Fraction  | 0.018  |

Figure 7 shows the user interface panel for control of membrane temperature. Control modes were developed to raise and lower the membrane temperature as determined by the current set point. The membrane temperature is lowered by opening a solenoid valve that

circulates liquid nitrogen ( $\text{LN}_2$ ) through the copper tube attached to the thermal shroud. The membrane temperature is raised by applying electrical power to the shroud heater. Heat is transferred between the thermal shroud and membrane under test through conductive, convective, and radiant heat flows.

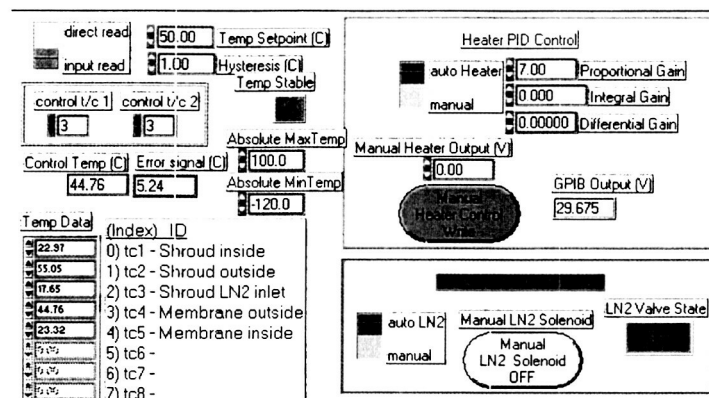


Figure 7 Membrane and Thermal Shroud Temperature Control Panel

The solenoid valve on the  $\text{LN}_2$  line is either open or closed, and requires a boolean signal for actuation. When the valve is open, cooling of the shroud occurs at a constant rate that is determined by the flow of  $\text{LN}_2$ . Alternatively, the electrical heater element warms the thermal shroud at a rate that is determined by the applied voltage, and uses a proportional control algorithm to affect temperature control. A unique control algorithm was developed to utilize these two opposite control modes to achieve the desired temperature set point. The algorithm functions by computing an error signal from temperature sensors located at different locations on the membrane. The sign of the error signal determines whether cooling or heating action is required, and the magnitude of the error signal determines the extent of the control action that is commanded.

If cooling is called for, the  $\text{LN}_2$  valve is opened and remains open until the measured temperature is within a range of the temperature set-point defined by the user input hysteresis value. If  $\text{CO}_2$  is present in the chamber, the temperature of the shroud and associated connecting tubing must not go below the freezing temperature of  $\text{CO}_2$  (-60 C), or else this gas will freeze on cooling the lines and change the relative composition and pressure of the chamber gas during experiments. This limits the practical lower temperature limit of the shroud and membrane to about -40C. If heating action is required to achieve the desired temperature set point, the error signal is transformed to a heater voltage value using a PID algorithm. The gains associated with the proportional, integral, and differential factors are set in the controls shown on the front panel. The computed voltage value is then sent to the heater power supply to effect thermal control. The software enables control of the membrane temperature within the range defined by the hysteresis (typically 1 degree C), over the temperature range from -40 to +100 C.

Similar control algorithms were developed for the total chamber pressure and chamber gas composition control loops. The  $\text{CO}_2$ , Ar, and  $\text{N}_2$  gas supplies are stored in high

pressure gas cylinders, each connected to the MTF through a separate pressure regulator and mass flow controller. The total pressure control loop uses the chamber pressure sensor as the input sensor, and provides a control signal to the CO<sub>2</sub> mass flow controller. A vacuum pump continually withdraws gas from the chamber, and constant pressure is achieved by controlling the CO<sub>2</sub> gas flow into the chamber through the mass flow controller. The gas composition control loop uses the Ar gas fraction measured by the mass spectrometer that is connected to the MTF chamber compartment as data input. The Ar gas fraction data is used to generate an error signal and compute a control signals for both the Ar and N<sub>2</sub> mass flow controllers. A separate mass spectrometer is used to measure the composition of the membrane permeate gas. A separate computer is dedicated for data acquisition and control of the two mass spectrometers. Gas composition data from each of the mass spectrometers is transferred from the mass spectrometer computer to the main MTF computer through a local network.

The mass spectrometers operate by bombarding the sampled gas with electrons to ionize the molecules. The ions are accelerated in an electrical field by an amount associated with the mass to charge ratio of the ion. Each mass spectrometer uses a different ionization potential, and shows a different cracking pattern, the cascade of molecular fragments and doubly charged molecular species that results from the ionization process. The cracking pattern for each mass spectrometer was characterized using pure CO<sub>2</sub>, Ar, and N<sub>2</sub> gases. CO<sub>2</sub> is ionized to CO<sup>+</sup> and O<sup>+</sup>, and shows molecular fragments at Atomic Mass Unit (AMU) 28 and 16. CO<sub>2</sub> is the predominant gas in the Mars atmosphere, but nitrogen (N<sub>2</sub>) is also present as a few percent, and also shows a value at AMU 28. This means that the total AMU 28 measurement value includes contributions from both carbon dioxide fragments and nitrogen. A correction algorithm was developed for each mass spectrometer to account for the interference from cracking, and generate correct values for the partial pressure of each gas species. Testing was performed to verify proper operation of the correction algorithms using a configuration where the MTF valves were actuated so that both mass spectrometers sampled the same gas. In this configuration the gas composition values measured by the two mass spectrometers agreed within 1%.

### MTF Characterization Experiments

The control loops provide a constant temperature, pressure, and gas composition environment in the MTF chamber gas compartment in which to characterize the gas separation performance of membranes. The CAM experiments involve measurement of gas permeation through membranes over a wide range of temperatures and pressures. A series of experiments were performed to tune the control loops and characterize the system. The experiments included instrument warm up to detect long term drift in the electronics, air and pure gas pressure control experiments, and thermal transient characterizations. Experiments were also performed using blank membrane support materials to determine relative flow characteristics under varying temperature and pressure conditions.

Preliminary experiments showed that the optimal experiment sequence for membrane characterization involves experiments that utilize a constant chamber pressure while systematically varying the temperature and trans-membrane pressure parameters. The experiment sequence may then be repeated over a series of total pressures to measure the membrane performance as a function of temperature and total pressure. This sequence is optimal because the time associated with a transient time between temperature set points is much shorter than the time for pressure transients. Using this approach, the overall experiment requires less time to complete than if total pressure were varied at constant temperature. Figure 8 shows the form of the experiments to characterize membranes over a wide range of temperatures and pressures.

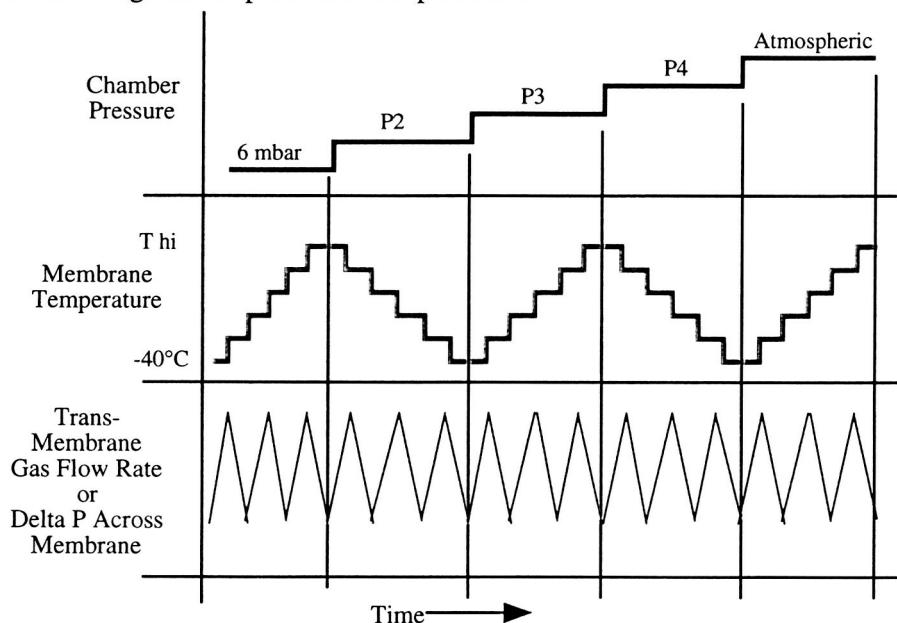
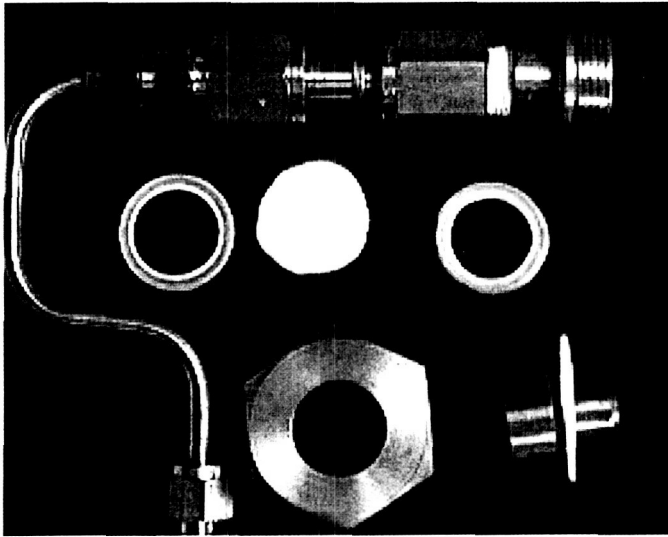


Figure 8 Systematic Membrane Characterization Experiment Sequence

### Thermal Control

The membrane is thermally linked to the MTF thermal shroud, and the membrane surface temperature lags behind that of the shroud, and is affected by the pressure, temperature, and gas composition in the MTF chamber. The lag presents a control challenge, especially at low temperature. The shroud cannot ever have a temperature lower than about  $-40^{\circ}\text{C}$ , because carbon dioxide ( $\text{CO}_2$ ) will freeze on the shroud surface and change the gas phase composition and total pressure in the chamber. The changing gas composition affects measurement of permeation because the presence of  $\text{CO}_2$  ice on the shroud affects the thermal coupling between the membrane and the shroud. The chamber total pressure also affects the membrane – shroud thermal coupling because of natural convection, increased gas pressure shows increased convective heat transfer. The membrane temperature is thus affected by many variables, and only indirectly controlled by the shroud temperature.

Two different membrane configurations are used in the MTF: planar and cylindrical, and each is coupled differently to the shroud. The planar membrane holder is a stainless steel inline filter holder that is coupled to the shroud as shown in Figure 9. The space between the filter holder and the thermal shroud is filled with silver plated copper braid material to increase the conductive thermal coupling.



*Figure 9 Planar Membrane Holder Interface with Thermal Shroud (photo)*

Cooling of the shroud occurs by flowing liquid nitrogen ( $LN_2$ ) through copper tubing attached to the shroud, and heating by applying voltage to a heater. The tubing and heater are spiraled together around the shroud, and attached using a copper plasma spray technique to increase the thermal contact. The control modes for heating and cooling in the MTF are different, boolean for cooling and proportional for heating. The  $LN_2$  flow is controlled with a solenoid valve that is boolean, either on to permit flow (and shroud cooling), or off where no cooling action occurs. Shroud heating is controlled by applying an electrical voltage to the heater that heats the shroud at a rate proportional to the applied power.

An improved thermal control algorithm was developed to facilitate control of membrane temperature. The algorithm uses fuzzy logic to implement control, with three discrete regions of control action defined as hysteresis ranges around the temperature setpoint. An error signal is computed based on the membrane temperature relative to the setpoint. The sign of the error signal determines the control mode (heating or cooling). The error signal magnitude determines the control region (course, medium, or fine). Each control region measures the temperature of the shroud and membrane surface, and uses different limits and control loop gains to command the thermal control actions. This approach allows the membrane surface temperature to be indirectly controlled via the shroud temperature using control of the liquid nitrogen solenoid valve, and electrical voltage applied to the shroud heater.



### *MTF Permeate Gas Volume Compartment*

The configuration of the membrane compartment volume was further developed to enhance the analysis capabilities. A sealed volume was defined for measuring gas permeation kinetics in the MTF. This volume is mostly outside the vacuum chamber in the tubing that connects the various valves and transducers, and is sealed to the membrane inside the chamber. Figure 10 shows a schematic diagram of the membrane compartment volume used in MTF experiments.

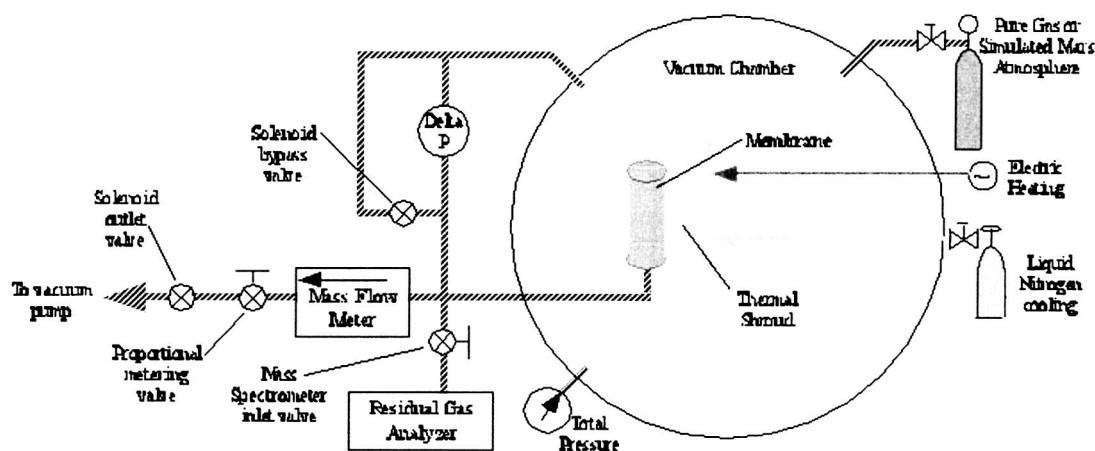


Figure 10 MTF Membrane Compartment Volume Schematic

### *Experiment Methods Development*

Scripting capability was developed to automate the membrane characterization experiments. The scripts allow automated sequencing of valves, setting of temperature and pressure control loop set-points, and detection of steady state conditions. This approach allows the temperature and pressure parameters of an experiment series to be defined and documented, and insures repeatable valve sequencing. Scripts are executed as a series of interpreted commands that allow control of

Script commands were developed to sequence the valves and obtain data for measurement of the pressure transients across the membrane. The valve actuation sequences consist of first evacuating the membrane compartment volume, then sealing the volume and allow the delta pressure across the membrane to decay to zero. The delta pressure data is measured as it decays to zero, and used to determine gas permeance.

### Analysis Method for Measurement of Gas Permeance

Gas permeance through a membrane is a measure of gas flow through a membrane, and is the product of the solubility of the gas in the membrane and diffusion of the gas through the membrane. The permeance value describes the gas flux through a membrane that is normalized to the driving force per unit area and time. The value of this parameter varies for different gases, membranes, temperatures, and pressures, and provides the design



basis for membrane separations. The units of membrane permeance used in this analysis are defined in Equation [1].

$$\text{Permeance} = \frac{\text{mass flow rate}}{\text{Area} * \text{time} * \Delta P} \quad [=] \quad \frac{\text{standard cc}}{\text{sq.cm} * \text{sec} * \text{cmHg}} \quad [1]$$

Permeance is typically determined by measurement of gas flow through a membrane under steady state conditions. A related *materials* property is the permeability, which is defined as the permeance times the membrane thickness or as the mass flux normalized by the gradient in driving force. A new method has been developed to measure membrane gas permeance that is based on a transient analysis of a pressure decay dynamics into a known volume. The experiment uses a sealed gas compartment of known volume that is instrumented with a pressure gauge to allow measurement of the pressure transient. The method requires that the experiment described below be performed under constant temperature and pressure conditions. Figure 11 shows a schematic diagram of the experiment setup and defines the variables used in the analysis.

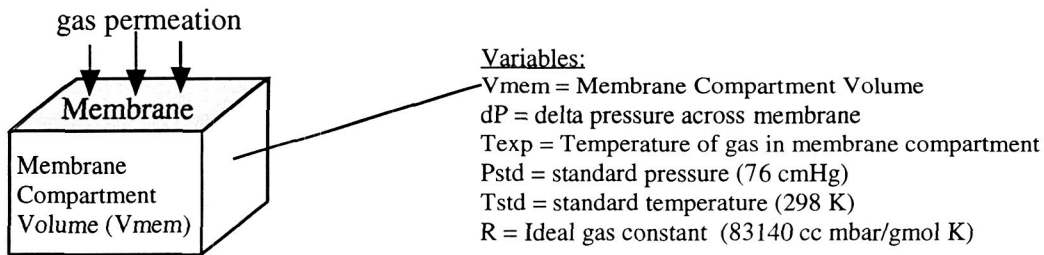


Figure 11 Gas permeation experiment setup and analysis variables

The experiment consists of evacuating the membrane compartment volume to create a difference in pressure across the membrane, and a driving force for gas permeation. The membrane compartment volume is then sealed, and the pressure allowed to equalize. The chamber volume is orders of magnitude larger than the membrane volume, and the pressure does not change during a permeation experiment. The pressure decay transient follows first order kinetics, and may be described by the exponential equation shown in [2]. Figure 12 shows the form of data that is measured in the experiment, and the exponential nature of the dynamics. The derivation of the permeation analysis equations is shown in Figure 13.

$$P(t) = ae^{-(t/\tau)} \quad [2]$$

$P(t)$  = Pressure decay transient as a function of time [mbar]  
 $a$  = fit coefficient [mbar]  
 $t$  = time  
 $\tau$  = exponential decay time constant [ $\text{time}^{-1}$ ]

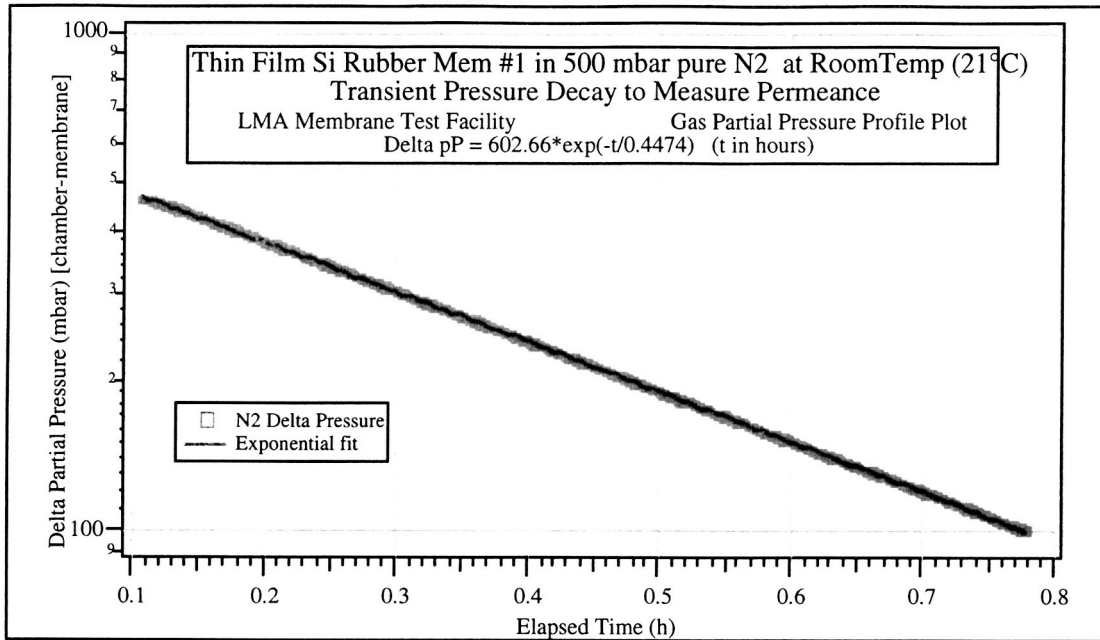


Figure 12 Exponential pressure decay transient data measured with pure nitrogen and a Polydimethyl silicone membrane at 21 C and 500 mbar total pressure.

#### Derivation of Permeance Measurement

1) Exponential fit to pressure decay transient

$$P(t) = ae^{-(t/\tau)}$$

$P(t)$  = pressure across membrane over time  
 $a$  = fit coefficient (mbar)  
 $t$  = time (hr)  
 $\tau$  = fit time constant ( $\text{hr}^{-1}$ )

[2]

2) determine first derivative of exponential pressure decay transient with respect to time:

$$\frac{dP(t)}{dt} = \frac{-a}{\tau} e^{-(t/\tau)} = \frac{P(t)}{\tau}$$

[3]

2) using ideal gas law ( $PV = nRT$ ) calculate molar gas flow through membrane:

$$\frac{dn}{dt} = \frac{dP(t)}{dt} \frac{V_{\text{exp}}}{R T_{\text{exp}}} = \frac{P(t)}{\tau} \frac{V_{\text{mem}}}{R T_{\text{exp}}}$$

[4]

3) convert molar flow rate to standard volume flow rate [scf]:

$$\dot{V} = \frac{dn}{dt} \frac{R T_{\text{std}}}{P_{\text{std}}} = \frac{P(t)}{\tau} \frac{V_{\text{mem}}}{R T_{\text{exp}}} \frac{R T_{\text{std}}}{P_{\text{std}}}$$

$$\dot{V} = \frac{P(t)}{\tau} \frac{V_{\text{mem}} T_{\text{std}}}{P_{\text{std}} T_{\text{exp}}}$$

[5]

4) calculate permeance:

$$\text{Perm} = \frac{\text{vol flow rate}}{\Delta P \text{ Area}} = \frac{\dot{V}}{\Delta P \text{ Area}} = \frac{P(t)}{\tau} \frac{V_{\text{mem}} T_{\text{std}}}{P_{\text{std}} T_{\text{exp}} \Delta P \text{ Area}}$$

[6]

$$\text{Perm} = \frac{V_{\text{mem}} T_{\text{std}}}{\tau P_{\text{std}} T_{\text{exp}} \text{ Area}}$$

[7]

Figure 13 Derivation of equations for permeance measurement analysis.

The exponential nature of the transient creates a fortunate circumstance for measurement of gas permeance through a membrane. A dimensional analysis of the permeance units

shows that the permeance value is defined by the standardized gas flux divided by driving pressure. Flow into the volume can be determined as the first derivative of the pressure transient. The first derivative with respect to time of an exponential equation is simply another exponential. Mathematical manipulation of these factors allows the exponential expression to cancel out of the analysis.

The result of this derivation is shown in the box around expression [7]. The equation shows that membrane permeance can be measured with six parameters, of which five are constant, defined either by standard conditions or the experimental setup. The units used for the constant parameters determine the units of permeance. Once the experiment conditions are defined, only the time decay constant ( $\tau$ ) is required for measurement of the membrane permeance. The decay transient may be measured over a long time to obtain high accuracy, and is a relatively easy measurement to perform. The analysis provides an overall measure of gas permeance that includes concentration polarization effects that may exist at the membrane surface. Table 2 compares pure gas permeance values measured with this new method with published permeance values measured under steady state flow conditions.

*Table 2 Comparison of Dimethyl Silicone membrane permeance values measured using transient method with published and independently measured values. Permeance units are [scc/s cm<sup>2</sup> cmHg]*

| Gas             | Mfr Literature* | Independent Measurement** | Transient Method |
|-----------------|-----------------|---------------------------|------------------|
| N <sub>2</sub>  | 7.1e-5          | 6.1e-5                    | 5.9e-5           |
| CO <sub>2</sub> | 7.7e-4          | 4.7e-4                    | 4.8e-4           |
| Ar              | 1.4e-4          | n/a                       | 1.2e-4           |
|                 | (25C 1015mb)    | (23C 810mb)               | (22C 500mb)      |

\*Literature from membrane manufacturer (Membrane Technology and Research Inc., Menlo Park, CA)

\*\* Independent measurement performed at Colorado School of Mines using steady state flow conditions in Tubular Membrane Permeation Cell (unpublished).

This method may be used to measure the separation characteristics of membranes in pure gases, or in mixtures of gases. In gas mixtures, the gas partial pressure transients must be measured over time, for example with a mass spectrometer to continually monitor the gas composition in the membrane compartment volume. Using this method with mixtures of gases allows membrane permeance measurements to be performed under actual operating conditions. This represents an end to end measurement of gas flux through the membrane that includes concentration polarization effects.

#### Development of Scripting Capability and MTF Experiment Protocols

A scripting capability was developed to automate the experimental procedure. The script is developed as a separate text file that contains instructions to perform sequential operations within the MTF. The scriptable operations include timing, actuation of solenoid valves, setting control loop set points for temperature, pressure, or flow, waiting

for the attainment of steady state in temperature, pressure, flow, or gas composition, or acquisition of steady state data to a high statistical confidence level. Looping capabilities were also included to enable systematic evaluation of membrane performance throughout a large temperature and pressure parameter space. Experiment scripts were written to initialize the system, perform delta pressure and flow measurements at constant chamber pressure and temperature, and iterate temperature in constant pressure conditions.

The parameter ranges for temperature, pressure, and membrane flow were defined as a series of discrete values. The experiment script uses these values as control loop set points in the MTF that are sequentially accessed during experiments. The data acquisition software also contains an algorithm to measure time variance of the data. Thresholds were defined for steady state conditions in terms of the data variability. During the transient phases between set points, the variability is high because the system is not at steady state. When a control loop is set to a given value, the system waits for steady state conditions to occur before proceeding further in the experiment protocol. Upon detection of steady state in terms of temperature, pressure, and flow, the software increases the data acquisition frequency, acquires a large number of measurements, computes the measurement mean and standard deviation, and stores the data in several data files. The control loop set points are then iterated and the cycle resumes. Upon completion of the script, a shutdown sequence is performed to terminate the experiment and execution of the program.

#### CAM Experiment Data Analysis

Software was developed to assist in analysis of CAM experimental data. The software is used in a post-processing mode to extract, reduce, and analyze pressure transient data measured in MTF experiments. Experimental data is graphically displayed to show parameter profiles for measured pressure, temperature, valve position, and gas composition. Figure 14 shows a typical experiment profile. The pressure transients for each temperature and pressure are extracted from this data for the permeance analysis. The plots show data from the pressure transducers and membrane flow meter (top plot), valve actuation state (2<sup>nd</sup> plot), temperatures throughout the MTF (3<sup>rd</sup> plot), and gas concentrations (bottom plot) in the chamber (dotted lines) and membrane compartment (solid lines).

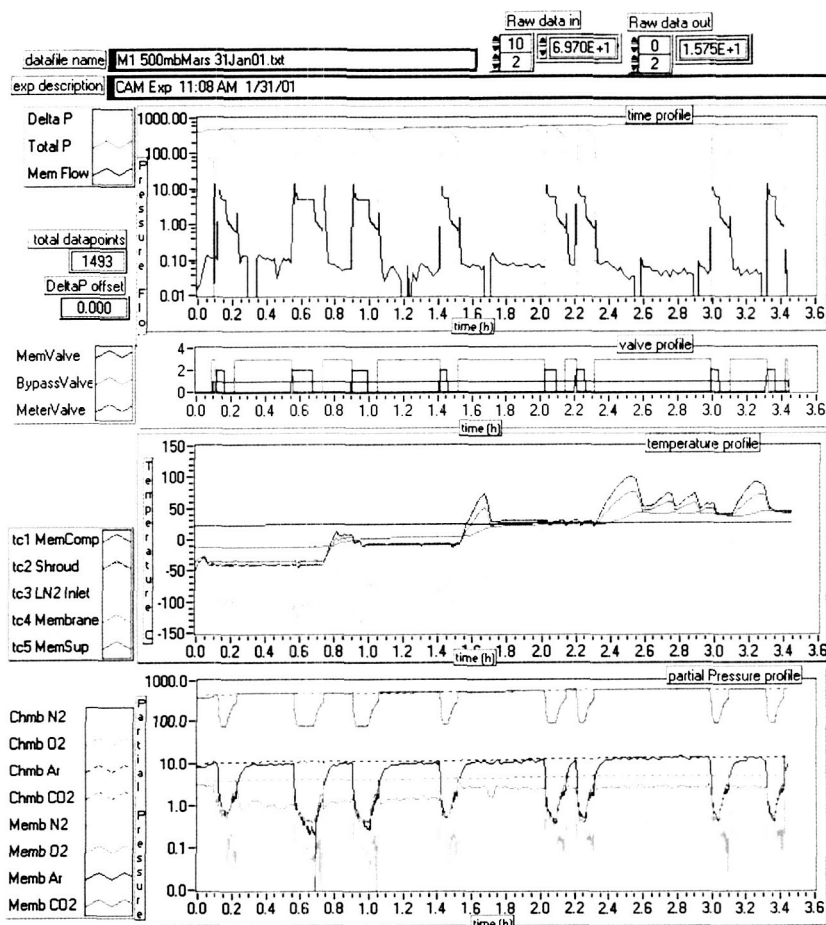


Figure 14 Typical experiment profile for permeance analysis.

Each transient event in the experiment represents a single permeance measurement that is identified, located, extracted, and analyzed. The analysis software to perform these calculations was developed based on the gas permeance analysis method described earlier in this report. Figure 15 shows the user interface for interactive performance of the permeance analysis procedure. All relevant parameters are either measured directly and averaged over the time interval (membrane temperature, total pressure, membrane compartment temperature), or input directly by the user (membrane area, membrane compartment volume). The time interval may be automatically identified by the valve sequences, or manually input by the user. The delta pressure transient data is displayed in the graph, along with an exponential fit to the data. The time constant determined from this analysis is used to calculate the membrane permeance based on the membrane area.

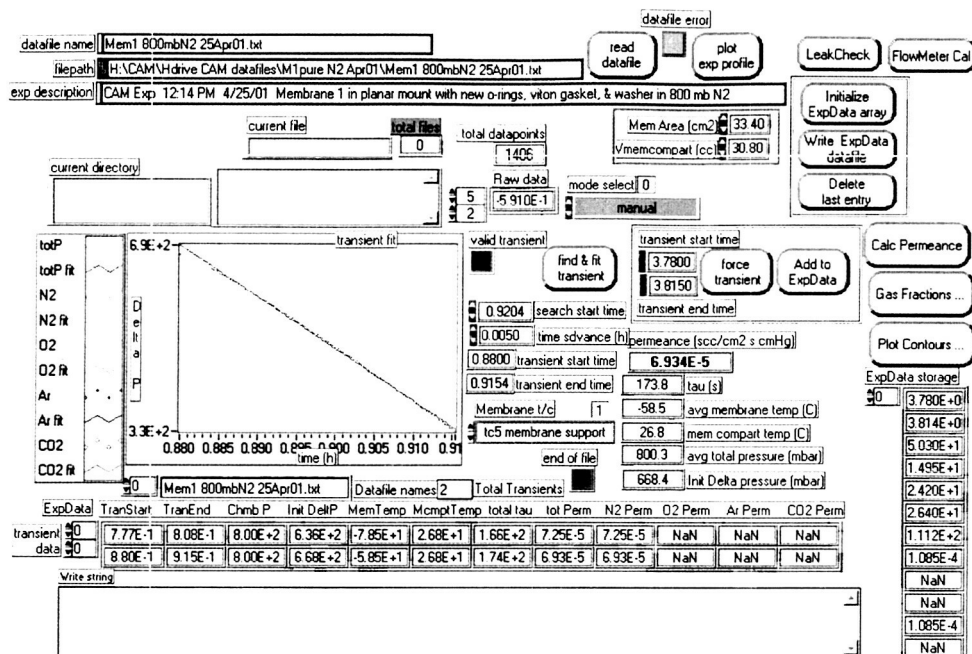


Figure 15 User Interface for Data Analysis Software

Permeance measured in the MTF is related to the time it takes for gas to fill a known volume (the membrane compartment) after a step reduction in pressure on one side of the membrane. The permeance value is determined by measuring the time constant associated with the pressure decay transient that occurs across the membrane. Figure 16 shows a typical pressure transient profile during the measurement of gas flow through a zeolite membrane. The initial increase in delta pressure is caused by evacuation of the membrane compartment using a vacuum pump connected through an exhaust valve. The exhaust valve is closed at the peak of the curve (time zero for the transient), and the pressure across the membrane decays toward zero as gas permeates into the sealed membrane compartment. The delta pressure decay transient is exponential, and shown as the linear segment on the semi-log plot.

Software was developed to compile the CAM experiment data, and perform analyses to summarize membrane permeance data over the range of temperatures and pressures tested. The analysis was developed to use the experimental data as the basis to interpolate membrane permeance data as a continuous function of temperature and pressure.

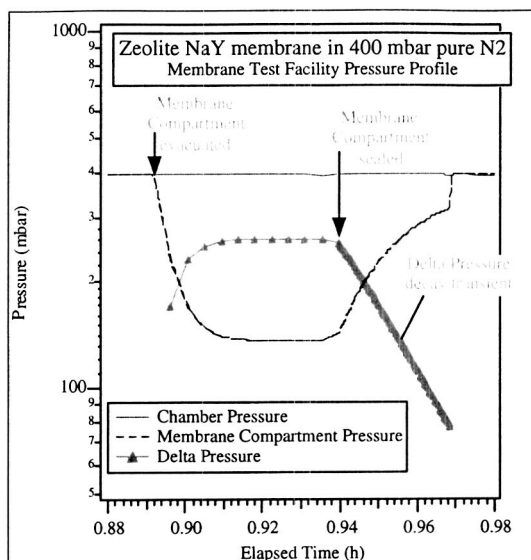


Figure 16 Pressure Profile During Permeance Measurement Transient

The experiments are performed as a series of pressure transients across the membrane while varying temperature, at constant pressure and gas composition. Figure 17 shows the form of the raw data from an experiment where the membrane temperature was varied under constant pressure conditions. The left plot shows temperatures in the MTF chamber and instruments, with ambient temperature in red, membrane temperature in blue, and the liquid nitrogen cooling inlet in green. The right side plot shows pressure and gas flow in the MTF chamber and membrane compartment. The total pressure in the chamber is constant during the tests (purple dashed line), the membrane compartment pressure in red, and the delta pressure across the membrane in green.

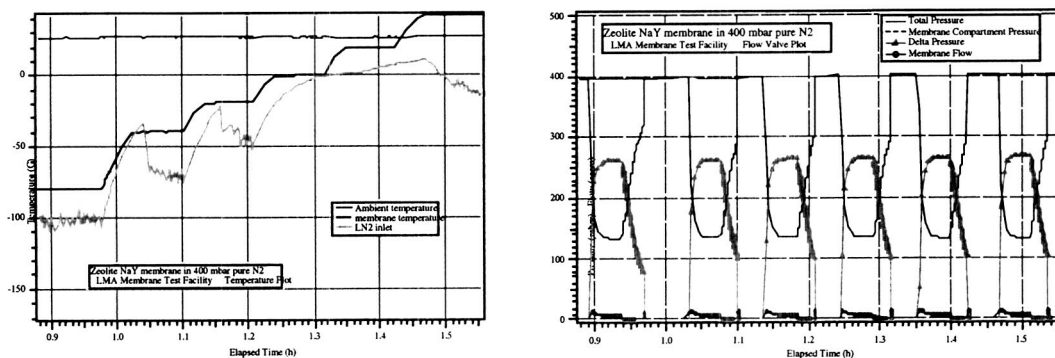
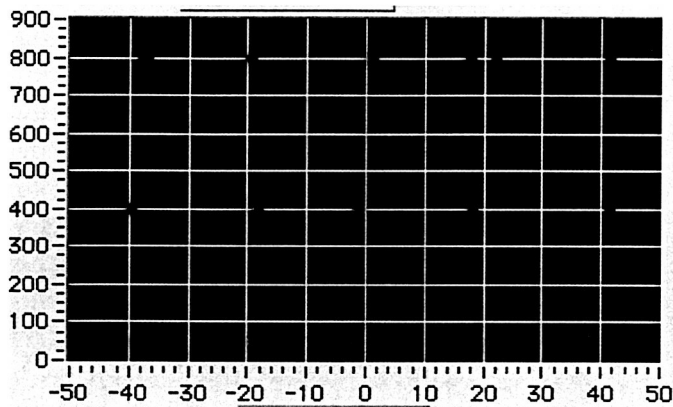


Figure 17 Raw Data from Temperature Series Experiment in Constant Pressure Environment. The left plot shows membrane temperature, and the right plot shows total pressure and trans-membrane pressure as a function of time.

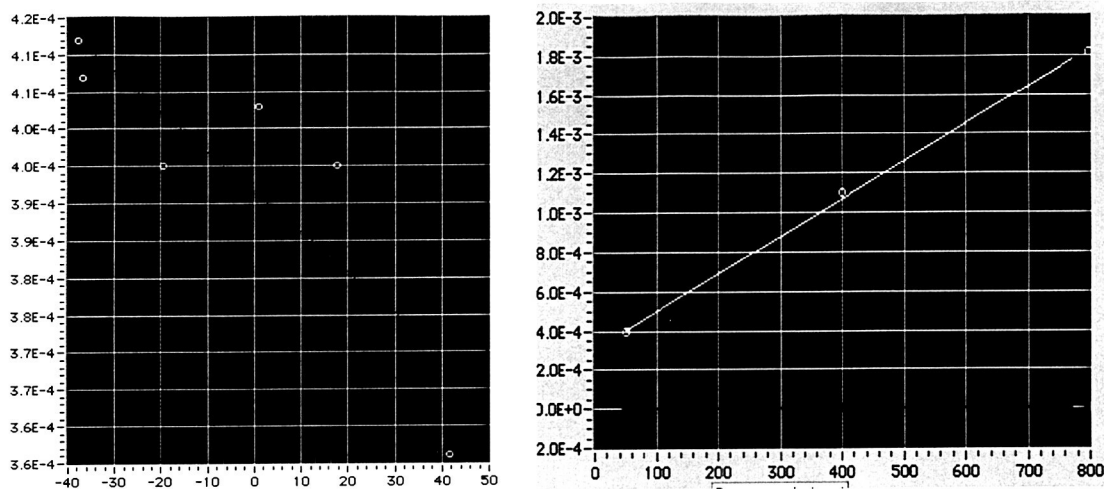
A series of these experiments are conducted at different pressures and in pure gas and mixed gas environments to determine how permeance is affected by temperature, pressure, and gas composition. Figure 18 shows a plot of the parameter space covered by a series of membrane experiments, where nitrogen permeance was measured through the PDMS membrane. Each point represents a specific temperature and pressure where permeance was measured. A similar series of experiments was conducted using the same membrane in pure argon, pure carbon dioxide, and simulated Mars environments.



*Figure 18 Typical Parameter Space Covered by Membrane Experiments in Constant Gas Composition Environment. Temperature is plotted on the x-axis, and pressure on the y-axis.*

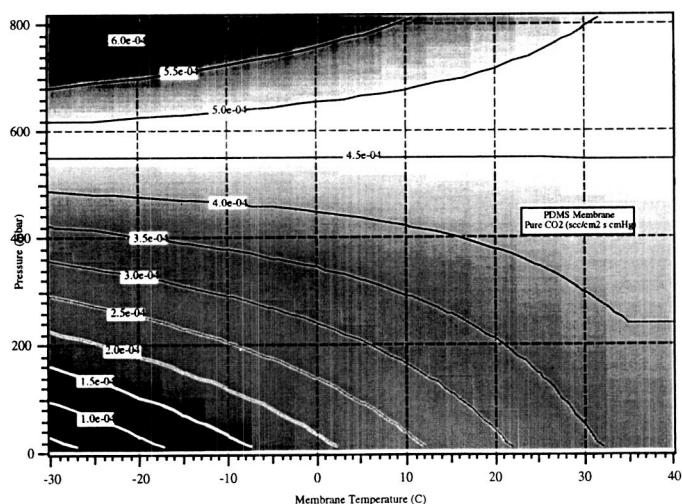
Each point on the plot shows where permeance value was measured in terms of temperature and pressure. A covariate analysis was developed to correlate these effects. The analysis performs a regression fit of the measured permeance values as a function of temperature, at constant pressure. The temperature fit coefficients are then analyzed in relation to total pressure, and another set of coefficients is obtained to predict the membrane permeance as a continuous function of temperature and pressure. Figure 19 shows typical regression fits that are performed to interpolate the data.





*Figure 19 Covariate Regression Analysis to Model Permeance in Terms of Temperature & Pressure. Left plot shows linear fit for gas permeance as a function of temperature. Right plot shows temperature fit coefficient as a function of total pressure.*

The result of this analysis is a function that predicts membrane permeance as a function of temperature and pressure for a specific gas. The data can be represented as a two dimensional matrix, with temperature as an independent variable along the graph x-axis, pressure as a second independent variable along the y-axis, and permeance as the dependent variable on the z-axis. The analysis results can be shown as a contour plot, such as in Figure 20 for CO<sub>2</sub> permeance through a PDMS membrane. The plot is color coded such that red indicates higher permeance, and blue is lower.



*Figure 20 Pure Carbon Dioxide Permeance in PDMS Membrane*

### Data Analysis of Mars Atmosphere Experiments

The permeance analysis technique was extended to include measured differences in constituent partial pressures of gas mixtures. The data is analyzed in a similar way to the pure gas case, except the partial pressure transients are used for each gas. The partial pressure transients are measured by a mass spectrometer that samples a small amount of gas from the membrane compartment during the pressure transient. A series of membranes was tested in this way with pure gases and Mars atmosphere mixtures to determine the pure gas and gas mixture selectivity for carbon dioxide relative to nitrogen and argon. This data gives an insight into the behavior of each gas when present in a mixture, such as that found in the Mars atmosphere.

Gas composition measurements using a mass spectrometer must be compensated for “cracking” of the gases, the ionic fragmentation of gas molecules that occurs when bombarded with electrons. This process causes carbon dioxide molecules to split and form carbon monoxide ( $\text{CO}^+$ ) and atomic oxygen ( $\text{O}^+$ ) ions. The molecular weight of CO is 28 (the same as nitrogen), creating an interference in the measurement of these masses. This measurement is made especially difficult when the nitrogen is present in small quantities relative to a large amount of  $\text{CO}_2$ , as occurs in Mars atmosphere. The relatively small proportion of mass 28  $\text{N}_2$  is swamped by the mass 28 CO that cracks from the  $\text{CO}_2$ . However, mass 14 is present in the data from  $\text{N}_2$  cracking, and follows the mass 28 nitrogen concentration well without interference, but the magnitude is much reduced. Another effect that is present in the data is the changing pressure of the membrane compartment, and the associated effects on molecular cracking. For these reasons, the nitrogen partial pressure measurement in the Mars atmosphere gas mixture is more uncertain than the other gases.

Algorithms were developed to correct the partial pressure data measured by the mass spectrometer sampling from the membrane compartment. The correction was based on cracking patterns observed for pure gases, applied to the partial pressures of each component. Data analysis routines were developed to apply the correction and determine the driving force across the membrane for each gas in the Mars atmosphere mixture as a function of time.

### **Membrane Test Facilities at Colorado School of Mines (CSM)**

The experimental apparatus used to test membrane permeance at CSM was designed to operate using pure gas at atmospheric pressure, not with mixed gases under reduced pressure conditions. In order to perform the mixed gas experiments, modifications had to be made in both our membrane cell and the gas flow system. The membrane cell is shown schematically in Figure 21 and the gas flow system in Figure 22. The changes to the membrane cell were necessary to operate the experiment using a He sweep gas on the permeate side to remove products and maintain a constant driving force. During permeation testing with a sweep gas, He was also added to the feed gas so that the partial pressure of He would be about the same in both the feed and permeate streams. The method will minimize back diffusion of He from the permeate side to the feed side of the

membrane. Modifications to the gas flow system included a gas mixing manifold as well as connection to an automated gas chromatograph to measure the composition of the residue and permeate streams. This modification allows gas mixtures to be tested under atmospheric pressure conditions.

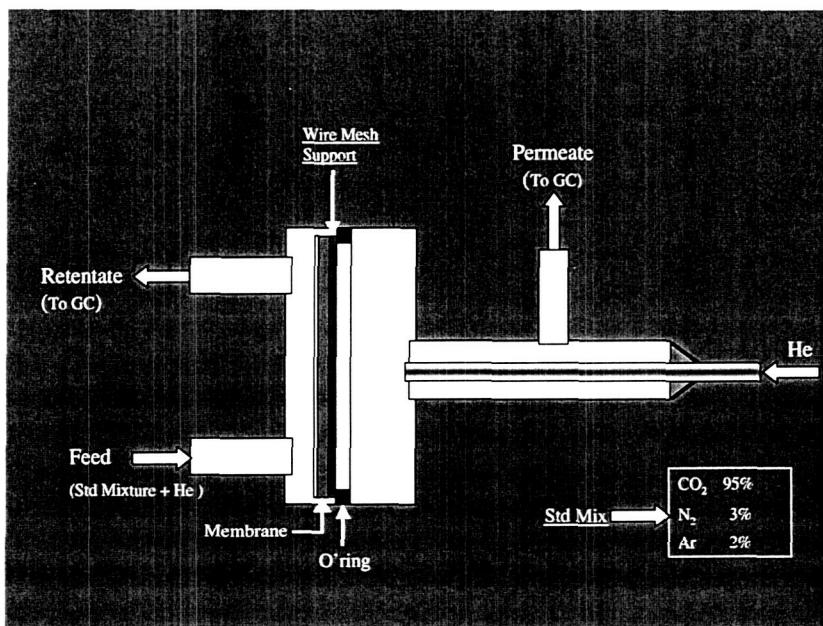


Figure 21. Schematic diagram of the membrane cell, modified for use with a sweep gas on the permeate side.

The Martian atmosphere contains approximately 95% CO<sub>2</sub>, 3% N<sub>2</sub> and 2% Ar. A standard mixture having this composition was used as the feed to the membrane cell in the mixture experiments. The mixed gas permeation studies were performed using three different modes of operation. The first mode consists of using the standard mixture and no sweep gas. The permeating gas flows from the membrane cell to the gas chromatograph and is analyzed. The second mode is to use a He sweep stream to flush permeating gases out of the cell and carry them to the GC for analysis. In this mode, He is added to the feed gas mixture so that the partial pressure of He is equal in both feed and sweep streams. Finally, in the third mode, the standard feed mixture is diluted with He to study the effect of CO<sub>2</sub> partial pressure on the mixture permeability.

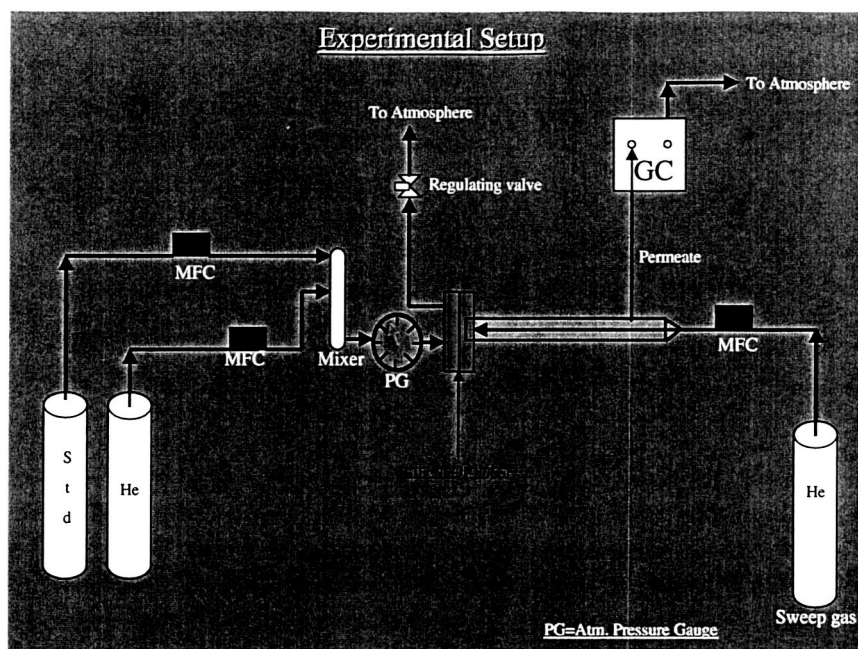


Figure 22. Gas flow system for mixed gas permeation measurements.

## Membrane Synthesis & Characterization Activities

A variety of membranes were identified and tested for permeance to CO<sub>2</sub>, N<sub>2</sub>, and Ar gases in pure and mixed gas experiments. The results of these activities for each membrane are summarized in the following sections.

## Membrane Evaluation Experiments

### Silicone Rubber Membrane

Several square feet of a commercial silicone rubber composite membrane (Poly DiMethyl Siloxane, PDMS) were obtained from Dr. Hans Wijmans of Membrane Technology and Research (MTR, Menlo Park, CA). This membrane has a 3.3 micron thick silicone rubber selective layer on a porous support fabric. According to MTR, the N<sub>2</sub> permeance (flux/delta P) of this membrane at room temperature and pressure is 70 GPU's or  $7 \cdot 10^{-5} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}$ . The O<sub>2</sub>/N<sub>2</sub> ideal separation factor (permeance ratio) at room temperature is 2.1.

The US subsidiary of Japan's Mitsui Engineering Company has provided us with a sample of their commercial faujasite zeolite membrane in the Na<sup>+</sup> form. The diameter of this tubular membrane is larger (12 mm) compared to the 1 cm OD tubes we have traditionally used.

### Silicone Rubber Membrane Permeation Test at Atmospheric Pressure

Pure gas permeation tests with CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> were performed with the MTR PDMS membrane over the temperature range -30 °C to 22 °C at a differential partial pressure of approximately 0.55 Bar. These tests were conducted using an apparatus at CSM, where the experimental temperature was limited to this range by the associated cooling device. Extrapolating our N<sub>2</sub> permeance data to 25 °C using an exponential fit, we obtain an N<sub>2</sub> permeance of 62 GPUs from our measurements. This is within 10% of the value specified by MTR. Our experimental O<sub>2</sub>/N<sub>2</sub> separation factor extrapolated to 25 °C is 1.94, within 8% of the MTR value. At this preliminary stage of the project, this is acceptable experimental error.

The CO<sub>2</sub> permeation data and the CO<sub>2</sub>/N<sub>2</sub> ideal separation factor are plotted against temperature in Figure 23. What is unusual is that both the CO<sub>2</sub> permeance and the separation factor increase as the temperature decreases. This suggests that the solubility of CO<sub>2</sub> in the silicone rubber membrane is increasing faster than the diffusivity is decreasing. This is further evidence of the synergistic effects of Martian ambient conditions on membrane transport. The PDMS membrane is more productive and more selective at the low temperatures that will be encountered in the Martian environment. Unfortunately, the combination of high CO<sub>2</sub> permeance and moderate CO<sub>2</sub>/N<sub>2</sub> separation factor was not observed during measurements with gas mixtures.

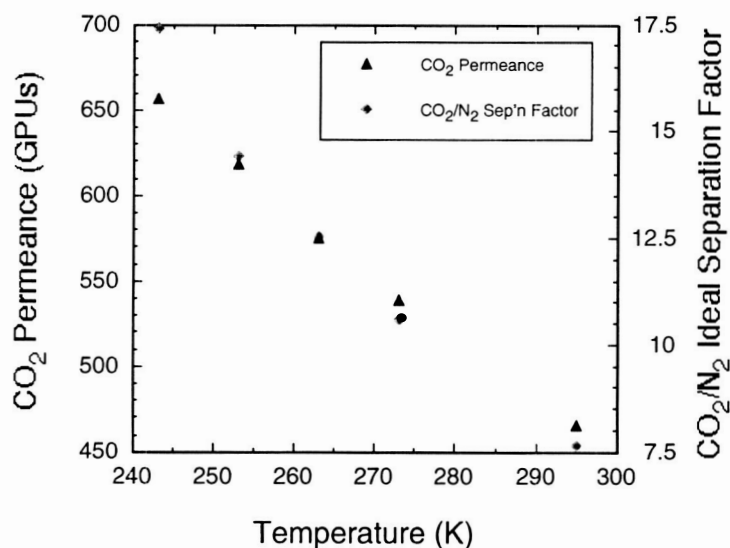


Figure 23. Effect of Temperature on the CO<sub>2</sub> Permeance and CO<sub>2</sub>/N<sub>2</sub> Permeance Ratio or Separation Factor. A gas permeation unit or GPU is  $10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}$ .

Since the solubility of the penetrants is likely to control the permeability of CO<sub>2</sub> in the PDMS membranes, it is important to perform permeation tests using gas mixtures. These experiments will reflect any competitive sorption behavior, and the separation factors obtained are likely to be different from those obtained with pure gases.

Pure and mixed gas permeation tests were performed with the MTR PDMS membrane over the temperature range 243 K to 298 K at a differential pressure of approximately 0.55 Bar. The ideal selectivity or pure gas permeability ratio of Ar/N<sub>2</sub> was previously reported to be 2.1 at room temperature in PDMS membranes (Robb, 1968). Experiments conducted at CSM showed an ideal Ar/N<sub>2</sub> selectivity of 1.75, consistent with the literature. Both Ar and N<sub>2</sub> show similar trends for their solubility and diffusivity coefficients and hence as temperature was changed, their permeability ratios remained almost a constant at 1.75. Since both these gases are non-interacting, relatively insoluble gases, the similarity in their behavior with temperature changes is expected.

However, the Ar/N<sub>2</sub> mixed gas separation factors were quite different than those measured for pure gases. Instead of being Ar selective, the PDMS membrane was N<sub>2</sub> selective for the mixed gas measurements. Over the temperature range 243 K to 298 K, the Ar/N<sub>2</sub> mixture separation factor was approximately 0.5. We believe this is due to competitive sorption where N<sub>2</sub> preferentially occupies free volume instead of Ar. These data are consistent with data from the MTF shown in Tables 3 and 4 below. The consequence of this behavior is that the CO<sub>2</sub>/Ar mixture separation factors will be twice those for CO<sub>2</sub>/N<sub>2</sub>.

Permeation tests with the MTR PDMS membrane using a feed mixture simulating the Martin atmosphere (95% CO<sub>2</sub>, 3% N<sub>2</sub>, and 2% Ar) were performed at CSM. These data are plotted in Figure 24 as a function of temperature with CO<sub>2</sub> partial pressure driving force as a parameter. These tests were intended to be screening tests prior to experiments at LM under actual Martian atmospheric conditions.

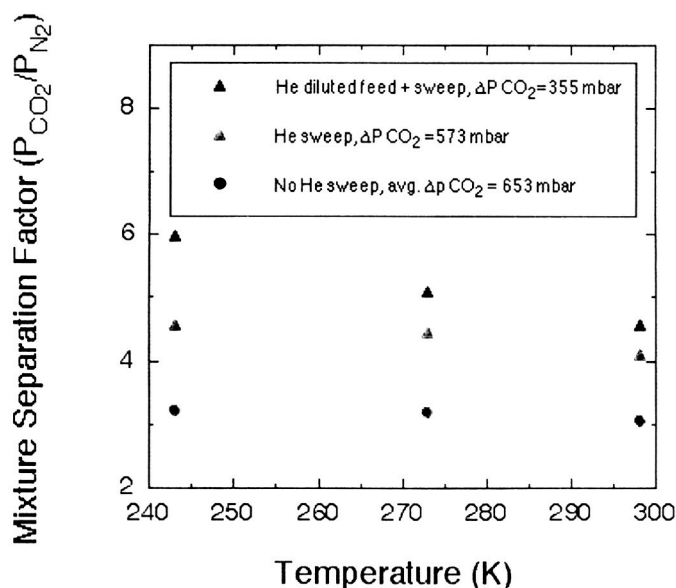


Figure 24. The influence of temperature on the CO<sub>2</sub>/N<sub>2</sub> mixture separation factor for the MTR PDMS membrane

In order to try to simulate partial pressure driving forces less than normal atmospheric pressure in Golden, CO of approximately 800 mbar, the CSM apparatus was operated using several different operating modes. The lowest CO<sub>2</sub> partial pressure difference of 355 mbar was achieved by diluting the feed mixture with He and using a He sweep gas on the permeate (product) side of the membrane. The intermediate CO<sub>2</sub> partial pressure driving force of 573 mbar was achieved using the Martian atmospheric gas mixture as the feed to the membrane cell and a He sweep gas. Finally, the highest CO<sub>2</sub> partial pressure driving force was achieved by using the Martian atmospheric mixture as the feed gas and no sweep gas. The permeate gas stream had a large enough flow rate to simply flow to the gas sampling valve on the gas chromatograph.

The separation factors measured for the mixture tests were up to a factor of three lower than those observed for the pure gas permeation tests. In general, the lower the CO<sub>2</sub> partial pressure difference, the larger the separation factors. The mixture separation factors ranged from 4.5 to 6 for the lowest CO<sub>2</sub> driving force as the temperature increased from 243 to 298 K. For the highest CO<sub>2</sub> driving force of 653 mbar, the separation factors increased from 3 to 3.2 over the same temperature range. The effect of temperature in the mixture permeation tests was that the separation factor increased as the temperature decreased. This effect was qualitatively similar to that seen in the pure gas tests.

The primary reason for the decline in the mixture separation factors for the PDMS membrane can be seen in Figure 25, a plot of CO<sub>2</sub> and N<sub>2</sub> mixed gas permeances measured at CSM. At a constant temperature of 243 K, the CO<sub>2</sub> mixed gas permeance is approximately constant at 155 GPU until the partial pressure driving force decreases to below 200 mbar. This average CO<sub>2</sub> permeance is significantly lower than the value of 650 GPU measured for pure CO<sub>2</sub> at 243 K and 550 mbar shown in Figure 23 above. However, the N<sub>2</sub> permeance measured at 243 K and 550 mbar partial pressure difference was 37 GPU, in reasonable agreement with the range of N<sub>2</sub> permeances in Figure 23 measured at low partial pressure differences. Therefore, the CO<sub>2</sub> mixed gas permeances were about a factor of four lower than the pure gas values. The possible reasons for this difference could be depression of CO<sub>2</sub> solubility in the membrane due to the presence of N<sub>2</sub>, Ar, or He or structural changes in the PDMS polymer at low temperatures. The glass transition temperature for PDMS is ranges from 233 to 243 K, very close to the lowest experimental temperature achievable by this atmospheric test device. A change from a rubbery state to a glassy state would greatly reduce the CO<sub>2</sub> permeability, which is consistent with the mixed gas permeation data. Data for two other rubbery polymers with very low glass transition temperatures will be presented below.



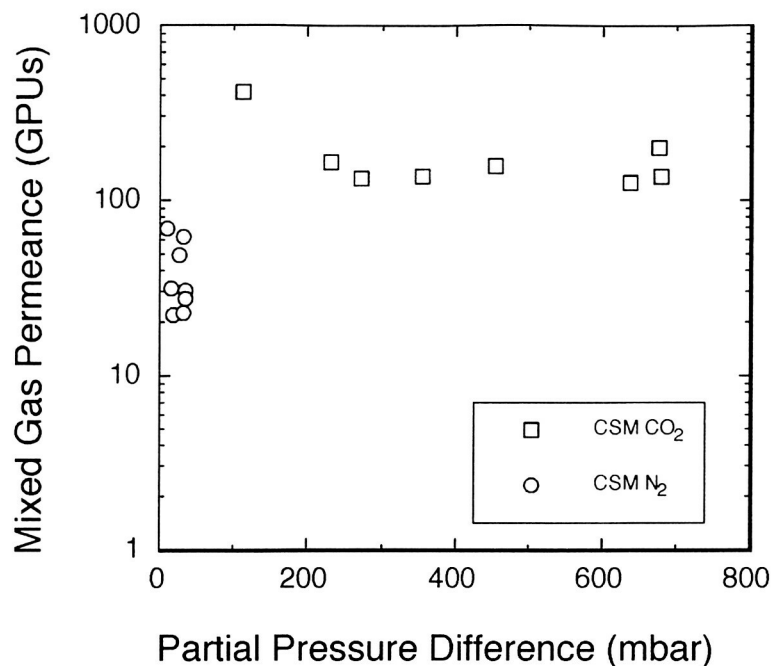


Figure 25. Effect of partial pressure driving force on the CO<sub>2</sub> and N<sub>2</sub> mixed gas permeances at 243 K

#### PDMS Membrane Tests in the MTF

The PDMS membrane is made of silicon rubber that is supported on a fabric substrate. Initial testing of this membrane was performed in the MTF under ambient and reduced pressure conditions using ambient air (21% oxygen and 79% nitrogen) in the primary chamber. The data shown in Figures 25-29 were acquired as part of the initial tests performed when the MTF was first put together, and some leaks were present in the system. Figure 26 shows the time profile for flow and pressure parameters during an experiment conducted at 500 mbar total pressure using room air as the chamber compartment gas.



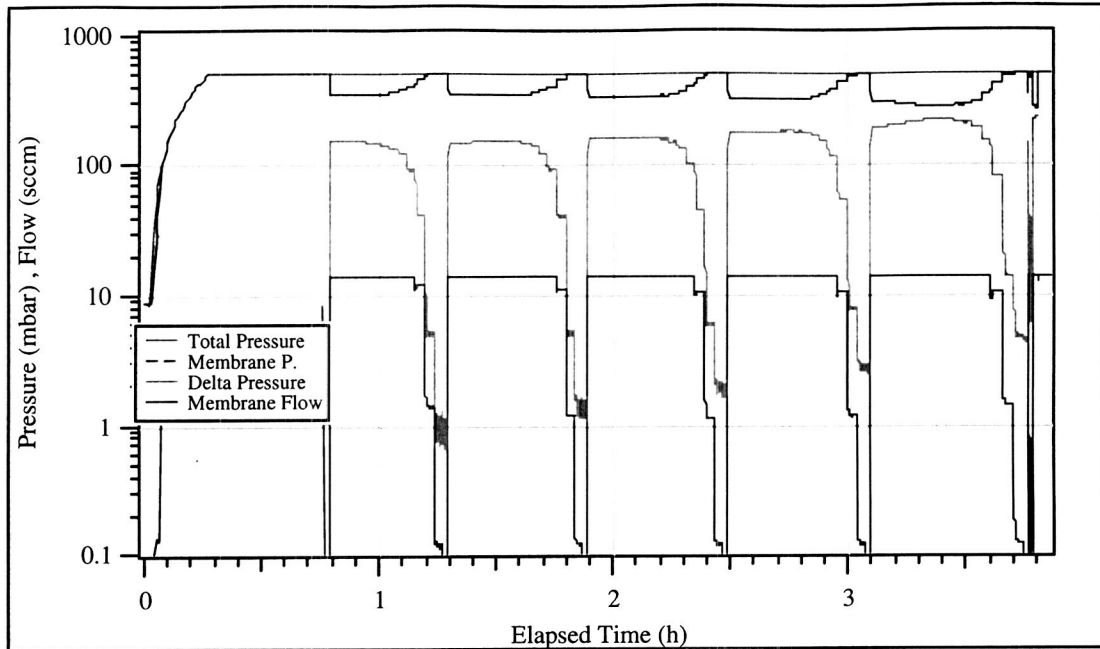


Figure 26 Time Profile of Flow and Pressure Values During Preliminary Experiment on Membrane #1 The total pressure was 500 mbar, and used room air.

Figure 27 shows the time profile for temperature, and Figure 28 shows the mole fraction of membrane permeate gas composition measured by the mass spectrometer during the same experiment.

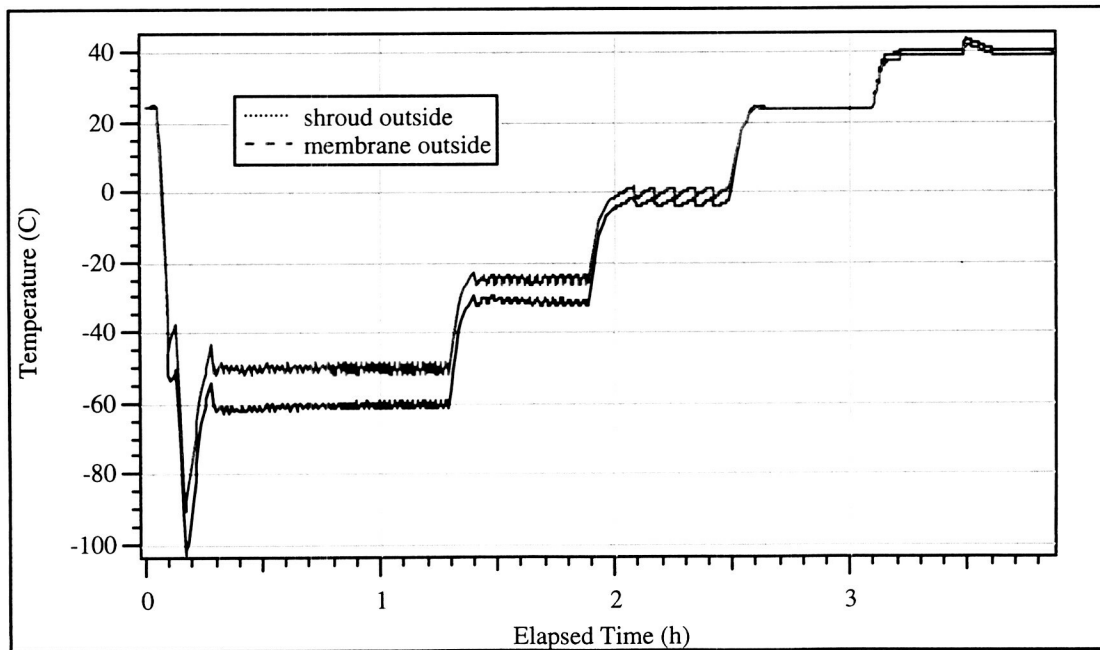


Figure 27 Time Profile of Membrane Temperature During a Preliminary Experiment on Membrane #1. The membrane was subjected to 5 different temperatures ranging from -50 C to +40C.

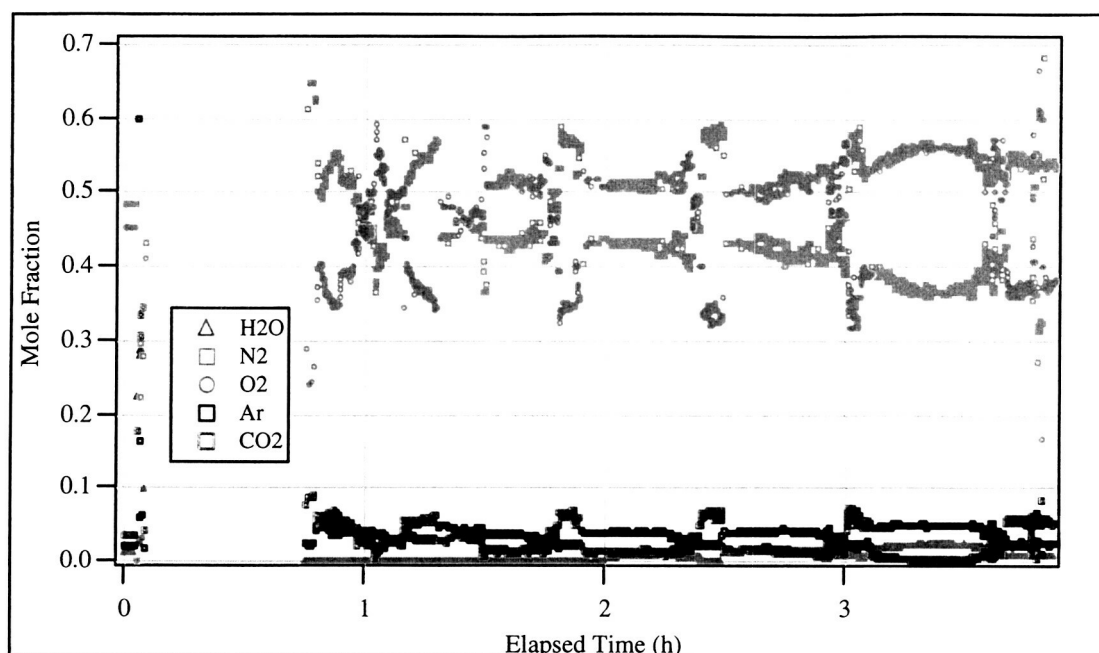


Figure 28 Time Profile of Membrane Permeate Gas Fraction During Preliminary Experiment on Membrane #1. .

Room air is composed of nitrogen (79%) and oxygen (21%), with trace amounts of argon and carbon dioxide. The results of this preliminary experiment show that the composition of the membrane permeate gas changed dramatically during the experiment. During each constant temperature period, the membrane delta pressure was varied over the range from 0 to 200 mbar, and the membrane permeate gas composition shows a difference in relative composition of the gases present, including an enrichment of CO<sub>2</sub>. The data shown in the profile plots are separated into five main segments that correspond to membrane temperature, with the coldest temperature first and the warmest temperature last. The CO<sub>2</sub> mole fraction data show that the warmest temperature (far right of plot) corresponds to the lowest CO<sub>2</sub> mole fraction in the permeate gas. This agrees with published literature for this membrane type that show higher solubility of CO<sub>2</sub> at lower temperature, and lower solubility at higher temperatures.

Analysis of the data acquired during the period of steady state temperature and pressure conditions was also performed. Figure 29 shows the membrane delta pressure and total trans-membrane gas flow rate as a function of the membrane valve position. Error bars are also included to show the low variability present in the measured parameters. The data show that the valve position directly affects both delta pressure across the membrane and gas flow rate through the membrane. The data show a transient phase that leads up to a maximum value for delta pressure and flow rate. This is expected as the membrane valve is incrementally opened, and higher delta pressure causes higher flow rates. The flow rate extends above what the data indicate, as the upper limit on this parameter is set by the flow meter itself. The data shown in the figure are for all 5 temperatures tested,

and the multiple values shown for maximum delta pressure indicate that the total membrane flow rate is a function of temperature.

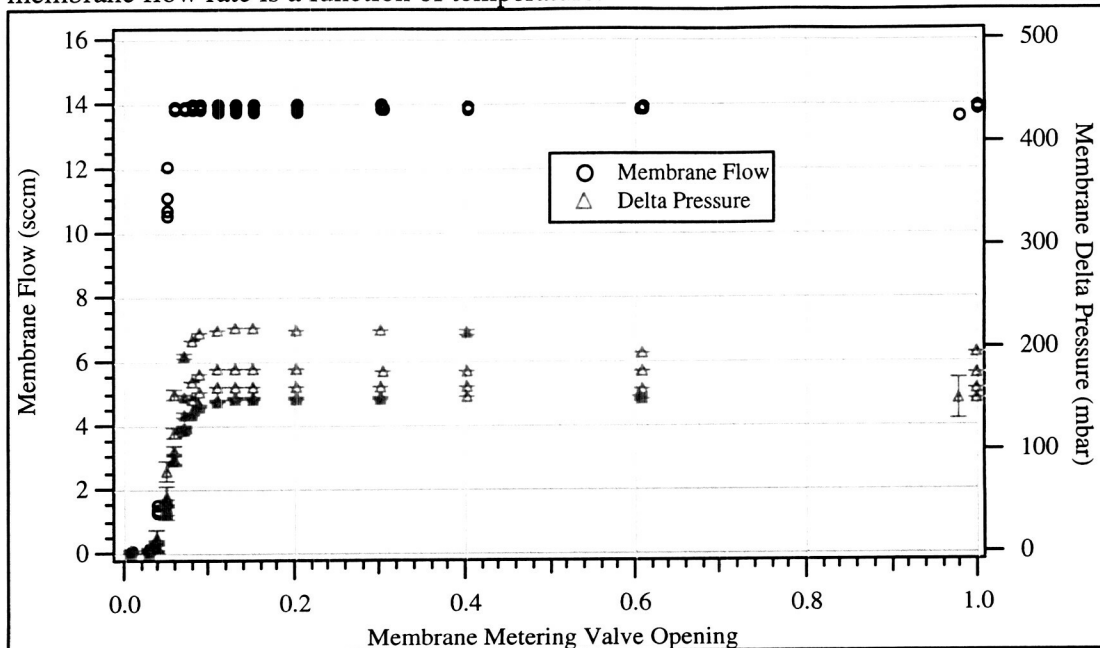


Figure 29 Membrane Permeate Gas Flow and Delta Pressure as a Function of Membrane Valve Actuation During Preliminary Experiments with PDMS Membrane.

Figure 30 shows a plot of viscous flow through the membrane (the total trans-membrane flow rate divided by the membrane delta pressure) as a function of delta pressure across the membrane.

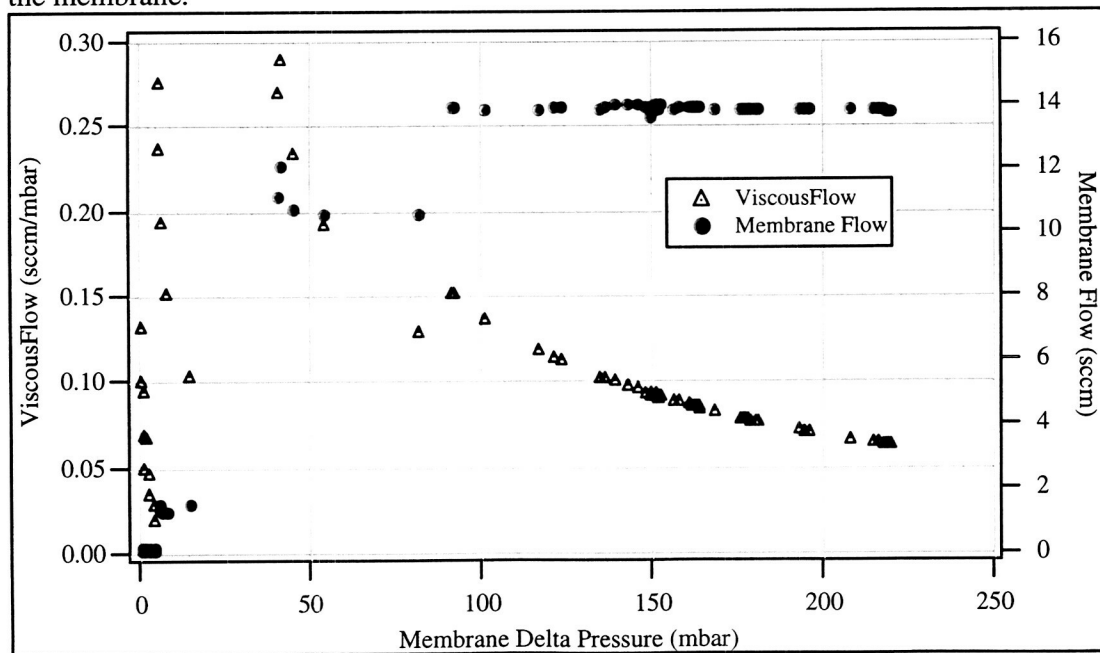


Figure 30 Normalized Membrane Permeate Gas Flow as a Function of Driving Force (Delta Pressure) During Preliminary Experiment on PDMS Membrane.

This plot shows that there was a leak present in the system. Trans-membrane flow data that has been normalized to the driving force (delta pressure) should show a constant value that is independent of the delta pressure, that is the data should show a slope of zero when presented in this way. The non-zero slope indicates that there was a leak in the system that resulted in bulk flow of gas originating either from the seal around the membrane, or the plumbing that comprises the MTF and associated gas compartments. Work is currently underway to identify and repair the leak.

Even though a leak was present in the system, these activities were useful for developing the system software, and provide an indication that the initial candidate membrane type shows higher permeability for CO<sub>2</sub> in mixtures of gases. The profile plot shown previously indicates that the membrane permeate gas composition changed dramatically during the experiment. The data from this experiment were used to calculate gas specific permeance values. These results are obscured by the presence of a leak in the system, but are still in reasonable agreement with published partition coefficients for this membrane type. This serves as a preliminary validation of the measurement approach used in the MTF.

#### PDMS Membrane Permeance

Data from the Poly-DiMethyl Silicone (PDMS) membrane experiments was analyzed, and the permeance determined as function of temperature and pressure. Table 3 shows the permeance measurement results for pure gases, and Table 4 shows the values for permeance in Mars atmosphere gases. The tables below show analysis results from permeance values measured at various temperatures and pressures, in pure gas and Mars atmosphere conditions. Temperature is shown in columns [deg C], pressure in rows [mbar], and permeance values are expressed in units of [scc/cm<sup>2</sup> s cmHg].

*Table 3 PDMS Membrane Permeance in Pure Gas (scc/cm<sup>2</sup> s cmHg)*

| pure Argon |          |          |          |          |          |
|------------|----------|----------|----------|----------|----------|
| Pres\Temp  | -40      | -20      | 0        | 20       | 40       |
| 10         | 8.46E-05 | 9.08E-05 | 9.70E-05 | 1.03E-04 | 1.09E-04 |
| 50         | 8.51E-05 | 9.10E-05 | 9.69E-05 | 1.03E-04 | 1.09E-04 |
| 100        | 8.57E-05 | 9.13E-05 | 9.69E-05 | 1.02E-04 | 1.08E-04 |
| 250        | 8.76E-05 | 9.21E-05 | 9.67E-05 | 1.01E-04 | 1.06E-04 |
| 500        | 9.07E-05 | 9.35E-05 | 9.63E-05 | 9.91E-05 | 1.02E-04 |
| 800        | 9.44E-05 | 9.52E-05 | 9.59E-05 | 9.67E-05 | 9.74E-05 |

| pure Nitrogen |          |          |          |          |          |
|---------------|----------|----------|----------|----------|----------|
| Pres\Temp     | -30      | -20      | 0        | 20       | 40       |
| 10            | 9.85E-05 | 9.07E-05 | 7.51E-05 | 5.96E-05 | 5.57E-05 |
| 50            | 9.75E-05 | 9.00E-05 | 7.48E-05 | 5.97E-05 | 5.59E-05 |
| 100           | 9.59E-05 | 8.87E-05 | 7.44E-05 | 6.00E-05 | 5.64E-05 |
| 250           | 9.12E-05 | 8.51E-05 | 7.29E-05 | 6.07E-05 | 5.76E-05 |
| 500           | 8.32E-05 | 7.89E-05 | 7.04E-05 | 6.19E-05 | 5.98E-05 |
| 800           | 7.36E-05 | 7.16E-05 | 6.75E-05 | 6.33E-05 | 6.23E-05 |

| pure CO2  |          |          |          |          |          |
|-----------|----------|----------|----------|----------|----------|
| Pres\Temp | -30      | -20      | 0        | 20       | 40       |
| 10        | 3.46E-05 | 8.58E-05 | 1.88E-04 | 2.91E-04 | 3.62E-04 |
| 50        | 6.53E-05 | 1.13E-04 | 2.08E-04 | 3.03E-04 | 3.69E-04 |
| 100       | 1.04E-04 | 1.46E-04 | 2.32E-04 | 3.17E-04 | 3.77E-04 |
| 250       | 2.19E-04 | 2.47E-04 | 3.05E-04 | 3.62E-04 | 4.02E-04 |
| 500       | 4.11E-04 | 4.16E-04 | 4.26E-04 | 4.36E-04 | 4.43E-04 |
| 800       | 6.41E-04 | 6.18E-04 | 5.71E-04 | 5.24E-04 | 4.92E-04 |

*Table 4 PDMS Membrane Permeance in Mars Atmosphere (scc/cm<sup>2</sup> s cmHg)*

| Mars Ar   |          |          |          |          |          |
|-----------|----------|----------|----------|----------|----------|
| Pres\Temp | -30      | -20      | 0        | 20       | 40       |
| 10        | 1.64E-05 | 1.64E-05 | 1.62E-05 | 1.61E-05 | 1.59E-05 |
| 50        | 1.93E-05 | 1.99E-05 | 2.10E-05 | 2.21E-05 | 2.32E-05 |
| 100       | 2.29E-05 | 2.43E-05 | 2.70E-05 | 2.97E-05 | 3.24E-05 |
| 250       | 3.37E-05 | 3.74E-05 | 4.49E-05 | 5.23E-05 | 5.98E-05 |
| 500       | 5.17E-05 | 5.94E-05 | 7.48E-05 | 9.01E-05 | 1.06E-04 |
| 800       | 7.33E-05 | 8.57E-05 | 1.11E-04 | 1.35E-04 | 1.60E-04 |

| Mars N2   |          |          |          |          |          |
|-----------|----------|----------|----------|----------|----------|
| Pres\Temp | -30      | -20      | 0        | 20       | 40       |
| 10        | 7.03E-06 | 6.68E-06 | 5.98E-06 | 5.28E-06 | 4.58E-06 |
| 50        | 1.77E-05 | 1.57E-05 | 1.18E-05 | 7.84E-06 | 3.90E-06 |
| 100       | 3.11E-05 | 2.71E-05 | 1.91E-05 | 1.11E-05 | 3.04E-06 |
| 250       | 7.11E-05 | 6.11E-05 | 4.09E-05 | 2.07E-05 | 4.83E-07 |
| 500       | 1.38E-04 | 1.18E-04 | 7.72E-05 | 3.67E-05 | 1.00E-07 |
| 800       | 2.18E-04 | 1.86E-04 | 1.21E-04 | 5.59E-05 | 1.00E-07 |

| Mars CO2  |          |          |          |          |          |
|-----------|----------|----------|----------|----------|----------|
| Pres\Temp | -30      | -20      | 0        | 20       | 40       |
| 10        | 4.34E-05 | 3.98E-05 | 3.25E-05 | 2.53E-05 | 1.81E-05 |
| 50        | 5.77E-05 | 5.36E-05 | 4.54E-05 | 3.71E-05 | 2.89E-05 |
| 100       | 7.57E-05 | 7.10E-05 | 6.14E-05 | 5.19E-05 | 4.24E-05 |
| 250       | 1.30E-04 | 1.23E-04 | 1.10E-04 | 9.62E-05 | 8.28E-05 |
| 500       | 2.20E-04 | 2.10E-04 | 1.90E-04 | 1.70E-04 | 1.50E-04 |
| 800       | 3.27E-04 | 3.14E-04 | 2.86E-04 | 2.59E-04 | 2.31E-04 |

Figure 31 shows the results for the CO<sub>2</sub> permeation through the PDMS membrane, in pure gas and Mars Atmosphere mixtures. Pure gas permeance measurements for Ar, N<sub>2</sub>, and CO<sub>2</sub> are shown in the top row, and for Mars atmosphere in the bottom row. The graphs colors are keyed so that red indicates higher permeance, and blue is lower permeance. Selectivity is defined as the permeance ratio of two gases through a membrane. This calculation was performed for both the pure gas and gas mixture

atmospheres. Figure 32 shows the gas selectivity of the PDMS membrane for each of the constituent gases in the Mars atmosphere as measured in the MTF.

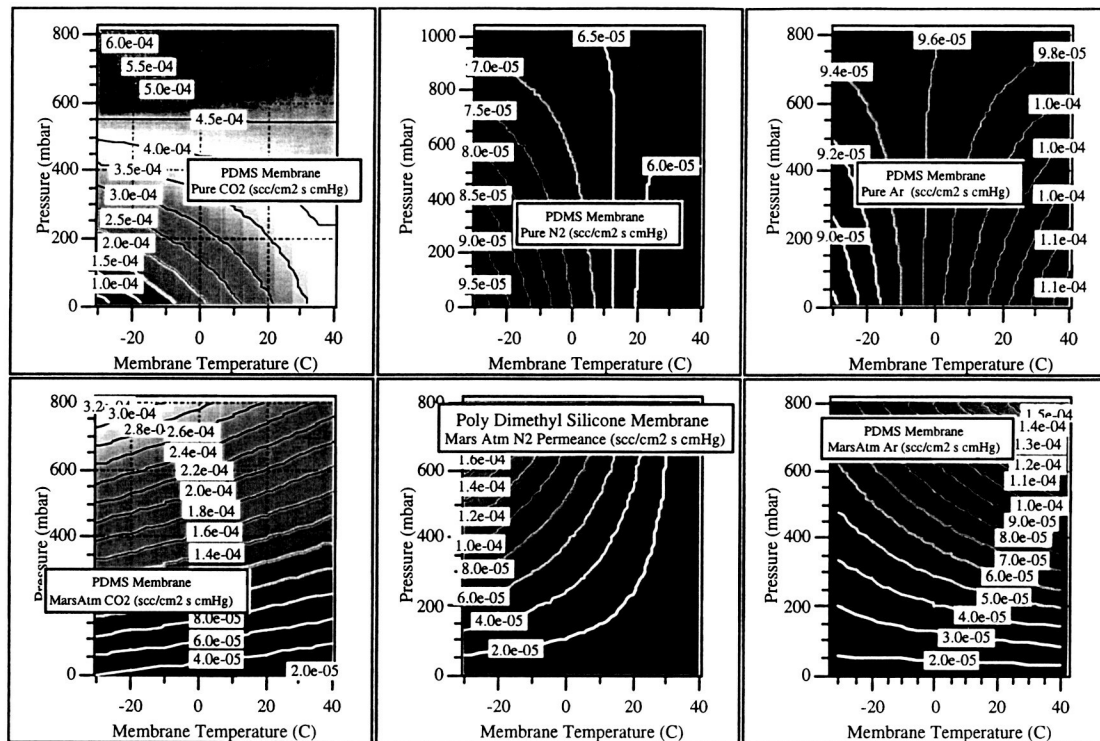


Figure 31 CO<sub>2</sub> Permeance Through PDMS Membrane in Pure Gas and Mars Atmosphere

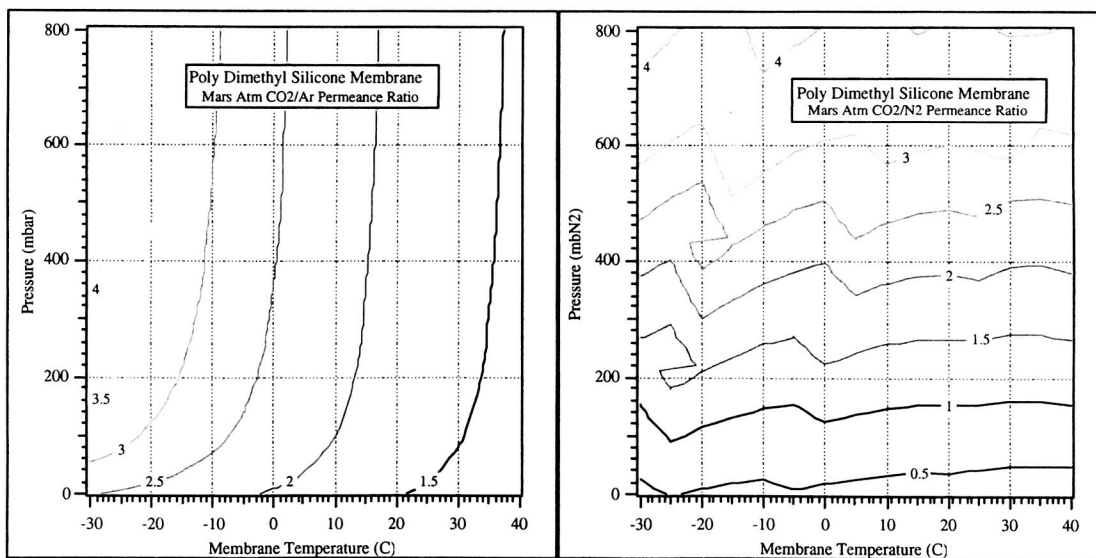


Figure 32 CO<sub>2</sub> Gas Selectivity of the PDMS Membrane in Mars Atmosphere

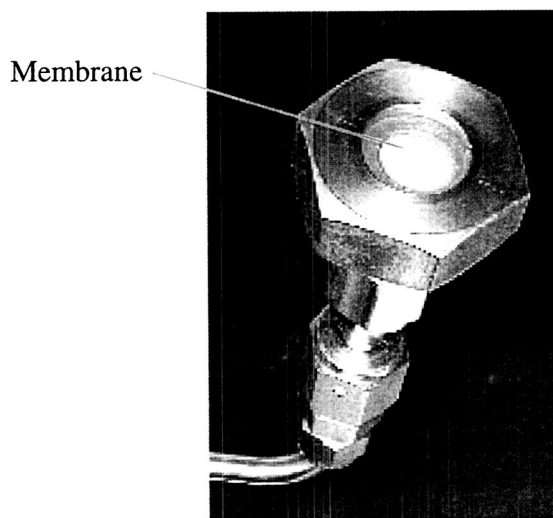
### *Conclusions from PDMS membrane Experiments*

In pure gas and Mars atmosphere environments, the PDMS membrane shows higher permeance for CO<sub>2</sub> than for Ar or N<sub>2</sub>. The best CO<sub>2</sub> / N<sub>2</sub> selectivity was obtained at low temperature (-30 C) and high pressure (800 mbar), with a permeance ratio of about 4. The (CO<sub>2</sub> / Ar) selectivity was found to be independent of temperature throughout the range -30 to + 40 C, and was highest in high pressure (800 mbar), where the maximum permeance ratio of 4 was measured.

The pressure transient for the Mars atmosphere gas mix was significantly altered by a Ar/N<sub>2</sub> boundary layer that formed in association with the membrane. This occurred in all membrane tests with Mars gases, and inhibited flow after a short period of time. The permeation analysis results shown here represent the maximum permeance value measured during the initial phase of the pressure transient. The effective permeance decreases as the boundary layer forms and inhibits diffusion of gas to the membrane surface. The membrane geometry plays an important role in the development and structure of the boundary layer.

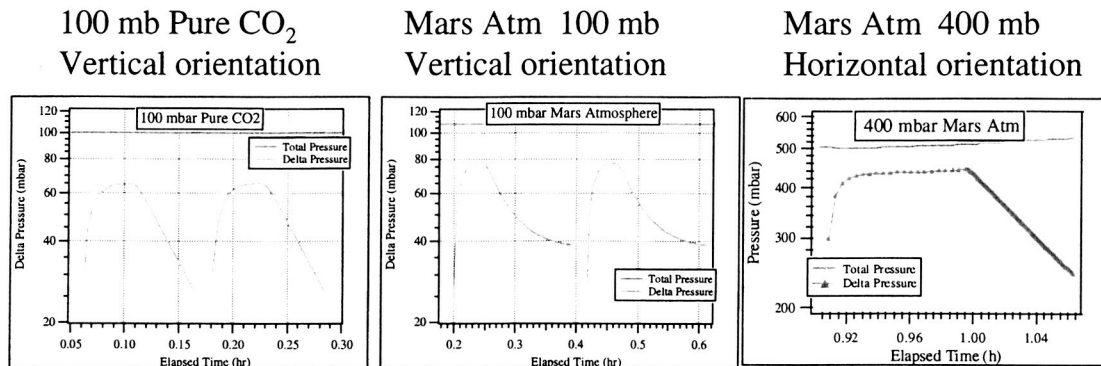
### Boundary Layer Formation in Mars Atmosphere Experiments

Membrane permeance kinetics were measured in pure gas and Mars atmosphere gas environments. The kinetics for these two cases can be significantly different, and also show a gravity orientation effect if the membrane geometry is enclosed. The membrane holder used for planar membranes creates a small cavity next to the membrane that can inhibit natural convection. The planar membrane holder used in these experiments is shown in Figure 33.



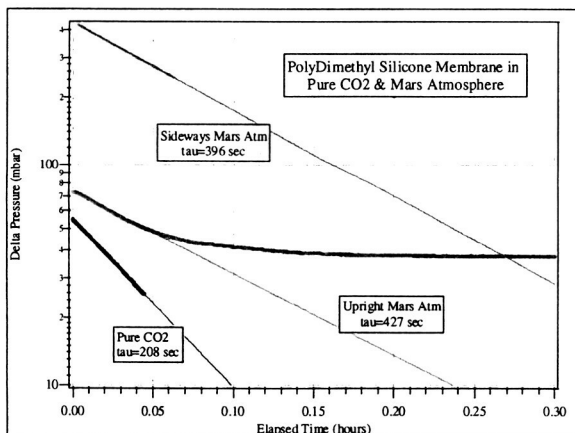
*Figure 33 Planar Membrane Holder Used for MTF Experiments*

Figure 34 shows data measured using the Poly-DiMethyl Silicone (PDMS) membrane in this support in pure CO<sub>2</sub> gas, and in Mars atmosphere gas mixtures, in vertical and horizontal gravity orientations.



*Figure 34 Pressure Decay Transients Measured for Pure CO<sub>2</sub> (left), Mars Atmosphere Vertical Orientation (middle), Mars Atmosphere Horizontal Orientation (right). Experiments performed using PDMS membrane at room temperature.*

The plot shows the pressure difference across the membrane as a function of time in pure gas (100% CO<sub>2</sub>) and simulated Mars atmosphere (95% CO<sub>2</sub>, 2.8% N<sub>2</sub>, 1.6% Ar). All of these measurements were performed at room temperature. The shape of the decay transients show that there are significant difference in kinetics of the pure gas and Mars atmosphere cases. Figure 35 shows these decay transients plotted together.



*Figure 35 Comparison of Pure Gas and Mars Atmosphere Pressure Transients for Two Gravity Orientations*

The pure gas case shows a pure exponential decay with a time constant of 208 seconds. The Mars atmosphere vertical orientation case shows a damped transient, with inhibited gas permeation where all gas flow *stops completely* after about 15 minutes. An



exponential fit to the initial part of the transient shows a pressure decay time constant of 427 seconds. The horizontal orientation in Mars atmosphere is undamped, but still shows a much longer time constant than the pure gas case, 396 seconds, even in a higher pressure environment. In both cases, the Mars atmosphere time constant is more than twice that of the pure gas case. The difference is caused by a buildup of  $N_2$  and Ar at the membrane surface that creates a boundary layer of gas. The boundary layer acts as a diffusion barrier to  $CO_2$ , decreasing the gas flow and increasing the time constant measured in these experiments. In Mars atmosphere, the boundary layer effect decreases the effective permeance of  $CO_2$ .

#### *Conclusions for membrane systems on Mars*

Total pressure and temperature affect the permeance dynamics. At higher pressures, the effective permeance of PDMS membranes to  $CO_2$  is reduced in simulated Mars atmosphere compared to pure gases. The inhibition is caused by concentration polarization effects from a boundary layer of the inert gases that develops next to the membrane. The relative permeance of  $CO_2$  is higher at low pressure than in the pure gas case, but still lower than the pure gas at higher pressure. The pressure effects are likely related to the increase in gas phase diffusion coefficient with decreased pressure. The higher diffusion inhibits the boundary layer formation. Solubility effects may also play an important role. These results indicate that membrane separations of Mars atmosphere gases may be more efficient at lower pressures. However, other factors must also be taken into account. The reduced pressure permeance value is lower than that seen at higher pressures with pure gas. In addition, the trans-membrane pressure difference that may be applied to a membrane is limited by the total pressure of the environment. Larger membrane areas will be required to offset the decreased driving potential available in a low-pressure environment.

In higher pressures, the presence of the inert gas boundary layer has significant design consequences for membrane systems to process Mars atmosphere gases. Membrane systems that collect these gases must be designed to minimize the thickness of this boundary layer. The boundary layer creates a diffusion barrier that inhibits gas phase transport of  $CO_2$  to the membrane surface. The geometry of such membrane systems should be designed such that the boundary layer formation is inhibited rather than enhanced. For example, the membrane should be fabricated such that it resides on an exposed outside surface rather than in an enclosed space.

Natural and forced convection can help minimize the boundary layer thickness. Mars gravity is about 3/8 that of Earth, and natural convection in gases is significantly reduced to that found on Earth. For this reason, natural convection on Mars will provide significantly less mass transfer capabilities than on Earth. Forced convection is also of limited utility in a low-pressure environment because of the low mass density.

#### Zeolite Membrane Synthesis and Permeance Analyses

Using the literature synthesis methods described by Morooka and coworkers (Kusakabe et al., 1997; Kusakabe et al., 1998a; Kusakabe et al., 1998b), we synthesized powders of the zeolite faujasite (FAU) structure type. SEMs of our powders and those from the literature

are shown in Figures 36 and 37 below. Our powders have the appropriate tetrahedral shape.

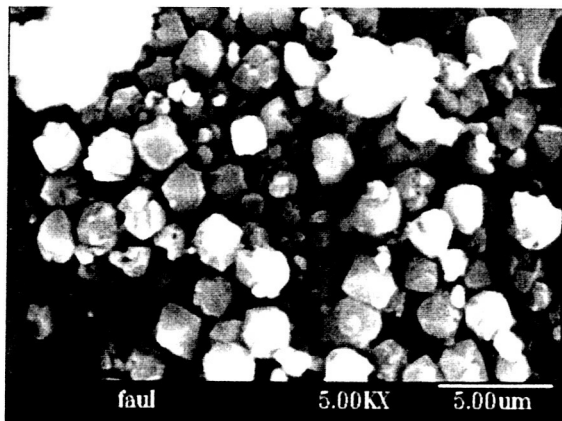


Figure 36. SEM of our faujasite (Type Y) zeolite powder

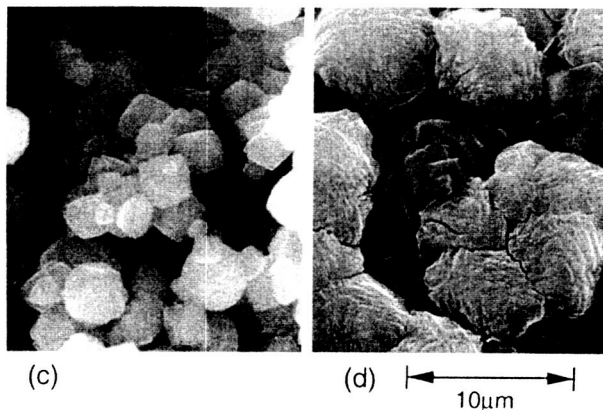


Figure 37. SEM from Kusakabe et al., *J. Membr. Sci.*, **148**, 13, 1998.

X-ray diffraction analysis confirms that we synthesized an FAU zeolite. As shown in Figures 38 and 39 below, the major peaks in our sample are also found in the XRD spectrum from the literature.

zeolite powder II

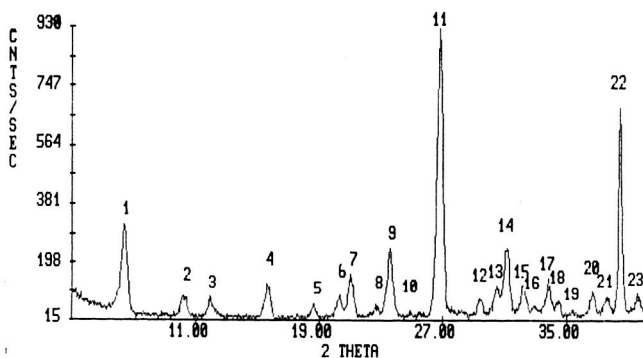


Figure 38. XRD pattern of our zeolite Y crystals

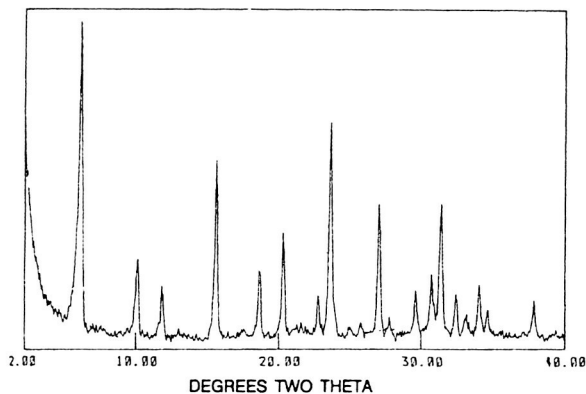


Figure 39. XRD pattern from Szostak, R., *Handbook of Molecular Sieves*, Van Nostrand Reinhold, NY, 1992.

### Zeolite Membrane Design Calculations

For transport of gases from binary mixtures, equation 1 can be derived for the minimum permeate mole fraction of inert gases present in the permeate CO<sub>2</sub> stream from a membrane module used for ISPP applications. This limiting case corresponds to zero CO<sub>2</sub> recovery and maximum purity. In equation 9 below,  $\alpha$  is the ideal separation factor, and  $x_o$  is the CO<sub>2</sub> mole fraction in the feed gas stream.

$$y_{p, \text{inerts}, \text{max}} = 1 - \frac{\alpha x_o}{\alpha x_o + (1 - x_o)} \quad [9]$$

Assuming the feed gas to the membrane process contains 95% CO<sub>2</sub>, equation 1 was used to estimate the minimum inert composition in the CO<sub>2</sub> permeate stream as a function of the ideal separation factor of the membrane material.

If the membrane material is silicone rubber, the CO<sub>2</sub>/N<sub>2</sub> ideal separation factor is approximately 20 at -30 °C. This corresponds to a N<sub>2</sub> composition in the permeate stream of 2600 ppm. Figure 40 below is good for quick screening of membrane materials, but an actual membrane module design calculation is necessary to determine the actual membrane area required as well as the flow rates and compositions of the residue and permeate streams leaving the membrane module.

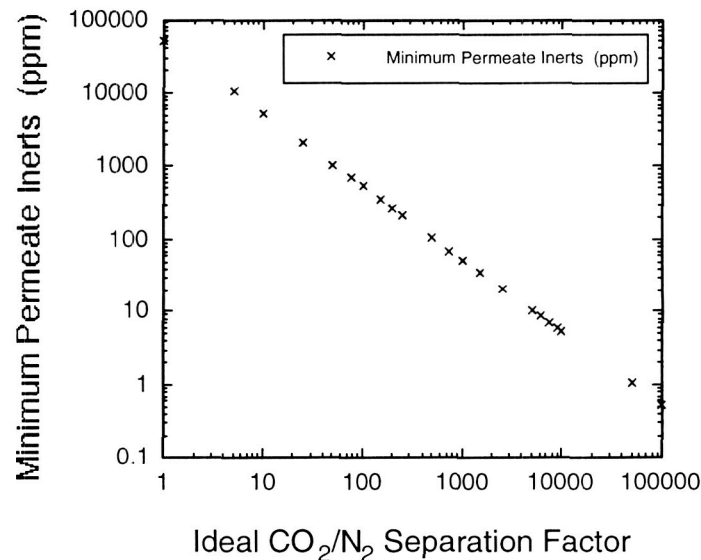
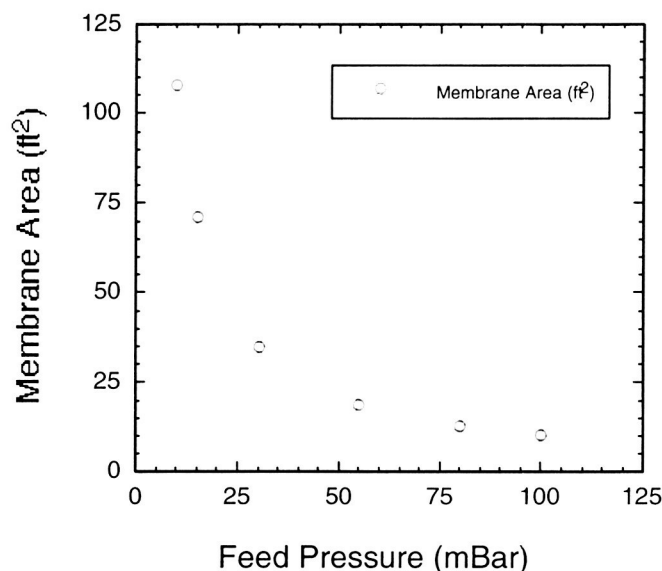


Figure 40. Effect of Ideal Separation Factor on the Minimum Inert Composition in the Permeate CO<sub>2</sub> Stream

Using the algorithms described by Shindo et al. (1985), a Mathematica function was written to perform membrane module design calculations for candidate ISRU systems at actual scale that may one day operate on the surface of Mars. For the base case, we used the permeability data for PDMS membranes above and calculated the membrane module area needed to supply 2.5 liters/minute of CO<sub>2</sub> to the ISPP process, assuming the feed pressure was 10 mbar, an average Martian atmospheric pressure, and the feed gas composition was 95% CO<sub>2</sub> and 5% N<sub>2</sub>. The permeate pressure was assumed to be 10<sup>-3</sup> mBar. The membrane area required for this separation is 108 ft<sup>2</sup>. This basis was chosen as that required to produce a CO<sub>2</sub> reactant stream for production of methane using the Sabatier Electrolysis process.

A series of design calculations were done by varying the feed pressure to the membrane module that ranges from 10 mBar to 100 mBar. As Figure 41 clearly shows, the required membrane area is very sensitive to the feed pressure, and drops from 108 ft<sup>2</sup> to approximately 10 ft<sup>2</sup> as the feed pressure increases. A scroll pump could be used to

increase the feed pressure substantially using very little power (several Watts). Assuming a module area/volume ratio of  $300 \text{ ft}^2/\text{ft}^3$ ,  $10 \text{ ft}^2$  of membrane area would have a volume of only  $0.035 \text{ cubic ft}$ . For example, for a module diameter of 3 inches, the module length would be only 8.5 inches. This case corresponds to 90%  $\text{CO}_2$  recovery and the  $\text{N}_2$  concentration in the permeate stream is 8000 ppm. This compares favorably to the minimum  $\text{N}_2$  permeate concentration of 2600 ppm calculated at the limit of zero  $\text{CO}_2$  recovery using equation 4.



*Figure 41 Effect of Feed Pressure on the Area of Silicone Rubber Membrane Required to Produce 2.5 liters/minute of  $\text{CO}_2$  Permeate from the Martian Atmosphere*

Progress has been made on the synthesis membranes. Using the literature synthesis methods (Kusakabe et al., 1997; 1998a; 1998b), We synthesized powders of our own  $\text{Na}^+$  faujasite (FAU) zeolite type having a Si/Al ratio of 9. X-ray diffraction analysis confirmed that we synthesized the FAU structure type zeolite. Using the standard literature nomenclature, this membrane is classified as a Y type FAU zeolite since the Si/Al ratio is greater than 1. We are using secondary growth methods to synthesize FAU zeolite membranes. In this method, porous alumina disk supports are seeded with small  $\text{Na}^+$  FAU crystals and the seeded membranes are sealed in an autoclave containing the synthesis solution. The idea is to encourage growth of the seed crystals to form a dense, inter-grown film. Several successive syntheses may be needed to form a selective zeolite membrane. Pure component  $\text{CO}_2$ ,  $\text{N}_2$ , and He transport data for two planar, FAU membranes supported on porous  $\alpha$ -alumina disks are given in Table 5. After two syntheses, the best mixed gas  $\text{CO}_2/\text{N}_2$  separation factor at room temperature was 2.85, which is 3.8 times the Knudsen diffusion separation factor for the  $0.2 \mu\text{m}$  meso-porous support. For transport through meso-porous membranes (pore size  $> 2 \text{ nm}$ ), the permeability ratio,  $\alpha_{ij}$ , can be calculated assuming Knudsen diffusion as:

$$\alpha_{ij} = \sqrt{\frac{MW_j}{MW_i}} \quad [10]$$

where MW is the molecular weight of the component. Both zeolite membranes described in Table 1 have CO<sub>2</sub>/N<sub>2</sub> selectivities greater than the Knudsen value. This suggests that selective adsorption and surface diffusion of CO<sub>2</sub> are responsible for the observed CO<sub>2</sub> selectivity. Based on prior molecular simulations (see Figure 42 below) and literature data, we expect the CO<sub>2</sub>/N<sub>2</sub> selectivity to increase at lower temperatures.

Table 5. CO<sub>2</sub>/N<sub>2</sub> Transport Data for CSM FAU ZeoliteY (Si/Al=9) Membrane at 298 K

| Membrane             | Gas Pair                        | Experimental Permeance Ratio (□) or Selectivity | Theoretical Knudsen Selectivity | CO <sub>2</sub> Permeance (mole/m <sup>2</sup> •Pa) |
|----------------------|---------------------------------|-------------------------------------------------|---------------------------------|-----------------------------------------------------|
| #9, 2 zeolite layers | CO <sub>2</sub> /N <sub>2</sub> | 2.85                                            | 0.76                            | 1.32•10 <sup>-8</sup>                               |
| #9, 2 zeolite layers | He/CO <sub>2</sub>              | 2.28                                            | 4.90                            | 1.32•10 <sup>-8</sup>                               |

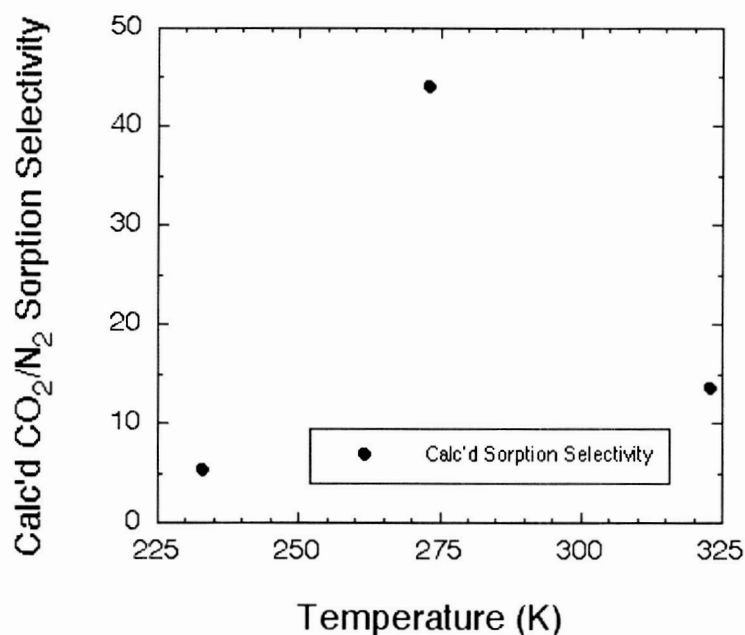


Figure 42. The influence of temperature on the calculated CO<sub>2</sub>/N<sub>2</sub> sorption selectivity for Na<sup>+</sup> zeolite Y. Sorption selectivity is ratio of adsorbed molecules normalized by partial pressure in gas phase. Simulations were performed using the Cerius2 software from Accelrys, Inc.

We have extensively investigated the application of faujasite zeolite membranes for the separation of CO<sub>2</sub> from the Martian atmosphere. Faujasite-type zeolite membranes were

grown on alpha-alumina supports, and subsequently characterized to determine transport and physical properties. The method of film growth was hydrothermal synthesis with seed crystals used to nucleate growth on the support surface. The membrane under consideration had four synthesis steps prior to full transport characterization studies being performed. The Si / Al ratio of the membrane was determined to be 1.42 +/- 0.04 via X-Ray diffraction (XRD) analysis. XRD was also used to verify that we had synthesized the faujasite zeolite structure. Transport studies were performed using the pure gases He, CO<sub>2</sub>, N<sub>2</sub>, Ar, Xe, SF<sub>6</sub>, and CH<sub>4</sub>, as well as a mixture of 95% CO<sub>2</sub>, 2.6% N<sub>2</sub>, and 2.4% Ar. The composition of this mixture is approximately equal to that of the Martian atmosphere. These studies were performed at a range of temperatures from -15°C to 100°C in the as-synthesized sodium ionic form, and in the ion-exchanged lithium and potassium forms as well. The observed selectivity was independent of ionic form or temperature. All gases smaller than Xe had Knudsen range selectivities when compared to each other.

*Table 6 Sodium Y Zeolite Membrane Characteristics*

| Table 3. Sorption and Permeation Membrane Characteristics |             |          |                   |            |          |
|-----------------------------------------------------------|-------------|----------|-------------------|------------|----------|
| Gas                                                       | Temperature |          |                   |            |          |
|                                                           | 25          | 0        | -15               | literature |          |
| pure gas permeance (mol/m^2*s*Pa)                         |             |          | Kusakabe Kumakiri |            |          |
| He                                                        | 4.89E-09    | 4.56E-09 | 4.77E-09          | 1.00E-07   | 2.00E-09 |
| He (N2sw)                                                 | 1.10E-08    | 6.54E-09 | 5.72E-09          |            |          |
| CO2                                                       | 2.14E-08    | 1.86E-08 | 1.00E-08          | 6.00E-07   | 2.40E-08 |
| N2                                                        | 2.53E-08    | 1.35E-08 | 1.24E-08          | 1.00E-07   | 1.30E-09 |
| pure gas selectivity                                      |             |          |                   |            |          |
| He/N2                                                     | 0.43        | 0.48     | 0.46              | 1.00       | 1.54     |
| He/CO2                                                    | 0.23        | 0.25     | 0.48              | 0.17       | 0.08     |
| CO2/N2                                                    | 0.84        | 1.37     | 0.80              | 6.00       | 18.46    |
| standard mixture permeance                                |             |          |                   |            |          |
| He                                                        | 2.91E-09    | 2.43E-09 | 3.53E-10          |            |          |
| CO2                                                       | 1.79E-09    | 1.04E-09 | 7.15E-10          |            |          |
| Ar                                                        | 2.16E-09    | 1.29E-09 | 9.31E-10          |            |          |
| N2                                                        | 2.19E-09    | 1.30E-09 | 9.28E-10          |            |          |
| standard mixture selectivity                              |             |          | Knudsen           |            |          |
| He/N2                                                     | 1.33        | 1.86     | 0.38              |            | 3.74     |
| He/CO2                                                    | 1.62        | 2.33     | 0.49              |            | 4.90     |
| CO2/N2                                                    | 0.82        | 0.80     | 0.77              |            | 0.76     |
| CO2/Ar                                                    | 0.83        | 0.81     | 0.77              |            | 0.91     |

Xe and SF<sub>6</sub> had Knudsen range selectivities when compared to each other; however smaller gases were favored over both of these at greater than Knudsen values. This suggests that Knudsen diffusion is a significant contributor to the observed transport, but that there also exists a molecular sieving transport effect that excludes the larger Xe and SF<sub>6</sub> molecules. This differed from previously reported results that strongly favor CO<sub>2</sub> over N<sub>2</sub>; a result that has been attributed to dominant surface diffusion effects. The reason for these differences is likely due to the presence of significant intercrystalline pathways of Knudsen-level size range in the membranes synthesized in this study. Research continues on both the characterization of the Mitsui tubular sodium Y

membrane, and the synthesis of a sodium Y membrane on a planar disk. The Mitsui tubular membrane exhibits  $\text{CO}_2/\text{N}_2$  selectivities on the order of Knudsen diffusion for both pure and mixed gases over temperature ranges from  $-15^\circ\text{C}$  to  $25^\circ\text{C}$ , shown in Table 6. This suggests that there are sufficient non-zeolite pores to negate any favorable sorption of  $\text{CO}_2$ . However, the transient behavior of  $\text{CO}_2$  as temperatures are changed does suggest that there is significant  $\text{CO}_2$  adsorption occurring.

Continual experimentation is underway on developing the best synthesis procedure for sodium Y faujasite. We are attempting to grow the film directly from seed crystals in solution under the assumption that this will result in a "purer" film than would likely result if the film were grown spontaneously on the porous disk. To decrease spontaneous crystal formation in solution (thus favoring crystal growth from the seed crystals), we use a more dilute solution, milder temperatures, and shorter times. This likely means that more repeated syntheses are necessary in order to achieve a selective zeolite membrane. Table 7 details the experimental data so far.

*Table 7 Sodium Y Zeolite Membrane Fabrication Variables*

| Gas                      | permeance   |              |              |             |             |
|--------------------------|-------------|--------------|--------------|-------------|-------------|
|                          | old disk    | new disk (1) | new disk (2) | new disk(3) | new disk(4) |
| He                       | 1.35E-07    | 3.62E-07     |              | 4.79E-07    | 3.78E-07    |
| $\text{CO}_2$            | 5.90E-08    | 1.59E-07     | 1.69E-07     | 2.71E-07    | 1.73E-07    |
| $\text{N}_2$             | 7.38E-08    | 8.61E-08     | 1.92E-07     | 2.89E-07    | 1.57E-07    |
| overtime (hr):           |             | 5.00         | 5.00         | 5.67        | 5.00        |
| rinsetime (hr):          |             | 0.25         | 0.25         | 18.10       | 12.00       |
| drytime (hr):            |             | 20           | 18           | 2.50        | 3.10        |
| wt (g):                  |             | 4.947        | 4.916        | 4.9119      | 4.9128      |
| delta wt:                |             |              | -0.031       | -0.004      | 0.001       |
| delta th (um): *         |             |              | -57.9808     | -8.3100     | 1.6431      |
| Selectivity              |             |              |              |             | knudsen     |
| $\text{CO}_2/\text{N}_2$ | <b>0.80</b> | <b>1.85</b>  | <b>0.88</b>  | <b>0.94</b> | <b>1.10</b> |
|                          |             |              |              |             | <b>0.76</b> |

(2)- used solution that was several weeks old and had apparent crystals growing in it. Possibly this caused "reverse" reaction.

(3)- used new solution, but also washed for twelve hours when done. This may be the cause of the increased permeance.

(4)- new solution, washed for 12 hrs.

(\*): a crude estimation of change in membrane thickness was calculated based on an assumed density of 1.5, which is the value for naturally occurring faujasite.

### Mitsui Zeolite Membrane

The US subsidiary of Japan's Mitsui Engineering Company has provided us with a sample of their commercial faujasite zeolite membrane in the  $\text{Na}^+$  form. Figure 43 shows results from permeance tests with this membrane in atmospheric pressure tests. The diameter of this tubular membrane is larger (12 mm) compared to the 1 cm OD tubes we

have traditionally used. Consequently, a new membrane holder was constructed as shown in Figure 44 below.

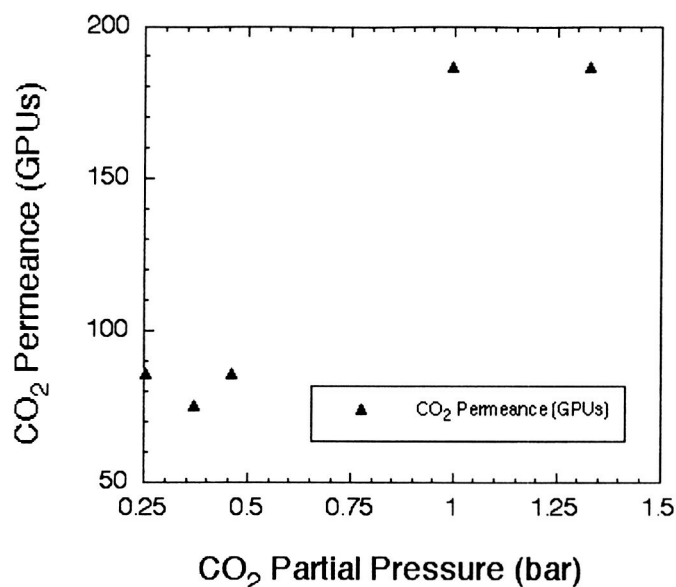


Figure 43. Effect of CO<sub>2</sub> feed partial pressure on the CO<sub>2</sub> for the PDMS membrane at 243 K. A gas permeation unit or GPU is  $10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}$ .

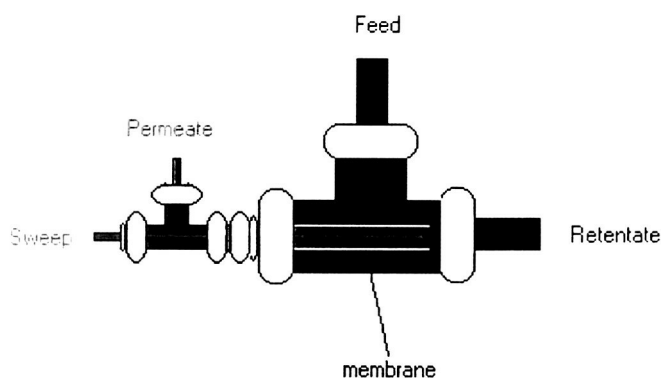


Figure 44. Schematic of the new holder constructed for the permeation experiments with the Mitsui zeolite membrane.

Preliminary pure gas permeation experiments were performed with the Mitsui zeolite membrane as received from the manufacturer at room temperature and compared with the literature (Kumakiri, 2000; Kusakabe et al., 1997; Kusakabe et al., 1998a; Kusakabe et al., 1998b). The membrane is a faujasite zeolite containing Na<sup>+</sup> as the counterion. Permeation measurements were done using He, CO<sub>2</sub>, N<sub>2</sub>, and SF<sub>6</sub> which have kinetic diameters (an equivalent spherical diameter) ranging from 0.26 nm to 0.515 nm. A plot of our data and those from the literature are given in Figure 45. The qualitative



relationship between permeance and molecular size for our data are essentially consistent with the literature. Our experimental CO<sub>2</sub>/N<sub>2</sub> ideal separation factor is 8, compared to 6 for the Kusakabe data and 24 for the Kumakiri data. The magnitude of the separation factors is consistent with a surface diffusion mechanism, suggesting that much higher CO<sub>2</sub>/N<sub>2</sub> separation factors will be seen at lower temperatures. If the transport mechanism was Knudsen diffusion, N<sub>2</sub> would permeate faster than CO<sub>2</sub>. The rather large differences in permeance are probably due to differences in membrane thickness and Si/Al ratio.

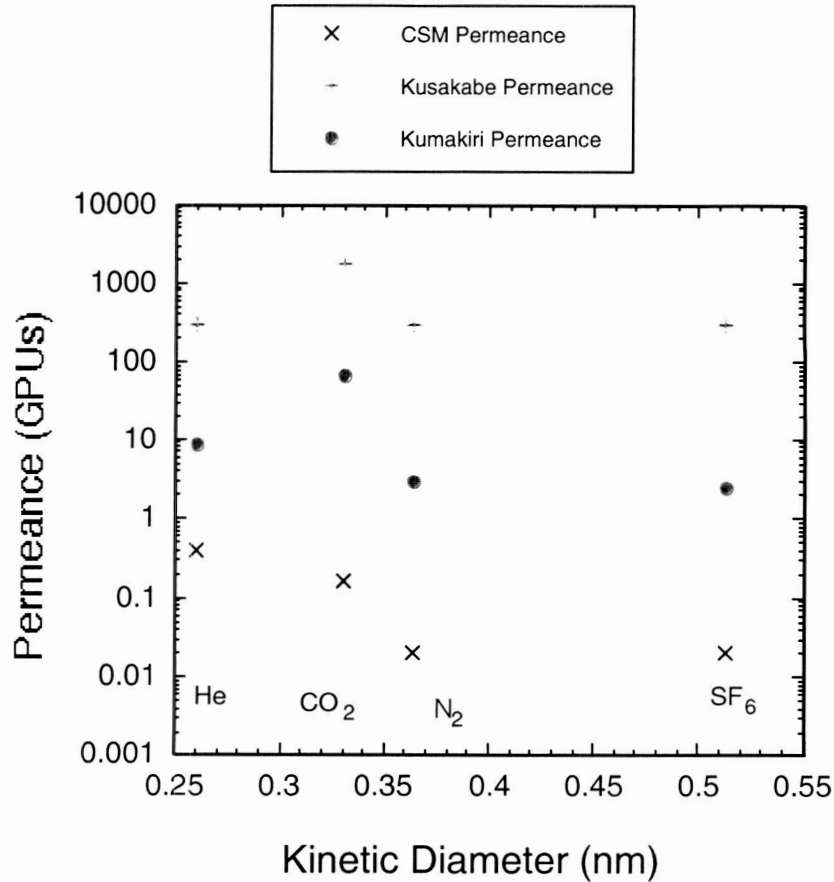


Figure 45. Effect of molecular size on the permeance for the Mitsui Na<sup>+</sup> form faujasite zeolite membrane. A gas permeation unit or GPU is  $10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}$ .

#### Zeolite Membrane Design Calculations

For transport of gases from binary mixtures, equation 1 can be derived for the minimum permeate mole fraction of inert gases present in the permeate CO<sub>2</sub> stream from a membrane module used for ISPP applications. This limiting case corresponds to zero CO<sub>2</sub> recovery and maximum purity. In equation 11 below,  $\alpha$  is the separation factor, and  $x_o$  is the CO<sub>2</sub> mole fraction in the feed gas stream.

$$y_{p, \text{inerts}, \text{max}} = 1 - \frac{\alpha x_o}{\alpha x_o + (1 - x_o)} \quad [11]$$

Assuming the feed gas to the membrane process contains 95% CO<sub>2</sub>, equation 11 was used to estimate the minimum inert composition in the CO<sub>2</sub> permeate stream as a function of the ideal separation factor of the membrane material.

If the membrane material is silicone rubber, the CO<sub>2</sub>/N<sub>2</sub> mixture separation factor is approximately 100 at -30 °C. This corresponds to a minimum N<sub>2</sub> composition in the permeate stream of about 500 ppm. Figure 46 below is good for quick screening of membrane materials, but an actual membrane module design calculation is necessary to determine the actual membrane area required as well as the flow rates and compositions of the residue and permeate streams leaving the membrane module.

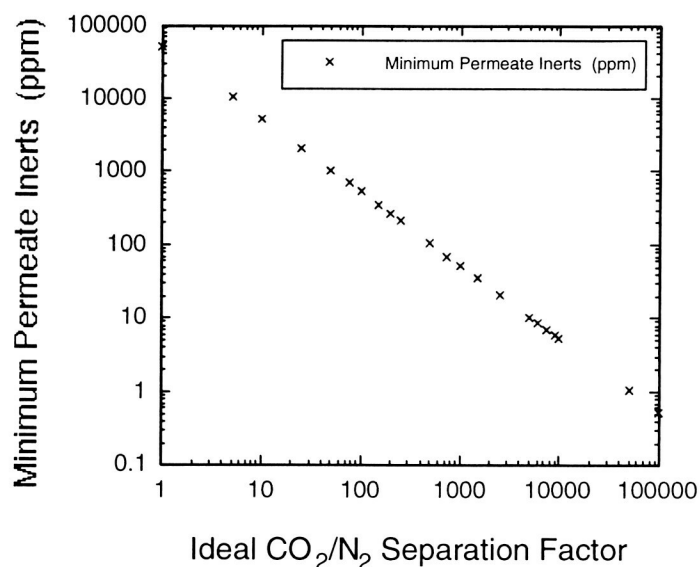


Figure 46. Effect of Separation Factor on the Minimum Inert Composition in the Permeate CO<sub>2</sub> Stream

#### MTF Experiment Results using Mitsui Zeolite Membrane

The Mitsui membrane is a commercially available zeolite thin film membrane supported on a cylindrical porous ceramic substrate, as previously described in the CSM progress section of this report. Figure 47 shows a photo of membrane #2 mounted in fittings that interface to the MTF.



*Figure 47 Mitsui Zeolite NaY Membrane Mounted in Flanges for Test in the MTF*

A simple experiment was devised for an initial quick look at the membrane permeance as a function of total pressure under constant (ambient) temperature conditions. The experiment consists of complete evacuation of the MTF chamber and membrane compartment. The valves are then positioned so that the membrane compartment is sealed, and the only gas path into the membrane compartment is through the membrane or a leak in the seal. Gas is then introduced into the chamber at a slow, constant rate, so the pressure rise in the chamber is linear with time. The delta pressure across the membrane is measured as a function of time. The membrane compartment pressure lags behind the chamber pressure by an amount directly related to the membrane permeance. This experiment provides a simple way to measure membrane permeance with a constant delta pressure over a wide range of total pressure.

In a membrane where permeance is independent of pressure, the delta pressure across the membrane remains constant. Figure 48 shows a simulation of this case that developed for comparison with measured data. A trace very similar to this was measured for membrane #1 in a no leak configuration. Test results measured with the NaY Zeolite membrane are shown in Figure 49. This experiment was performed at ambient temperature using pure Argon gas.

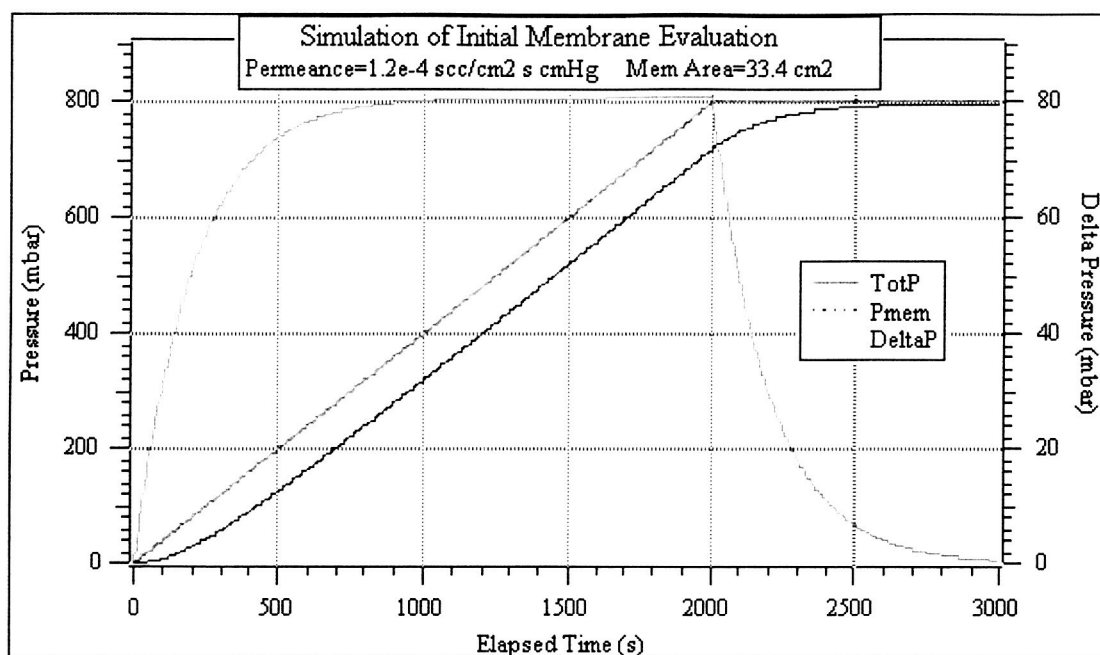


Figure 48 Model Simulation of Pressure Profiles Experiment used for Initial Evaluation of Membranes

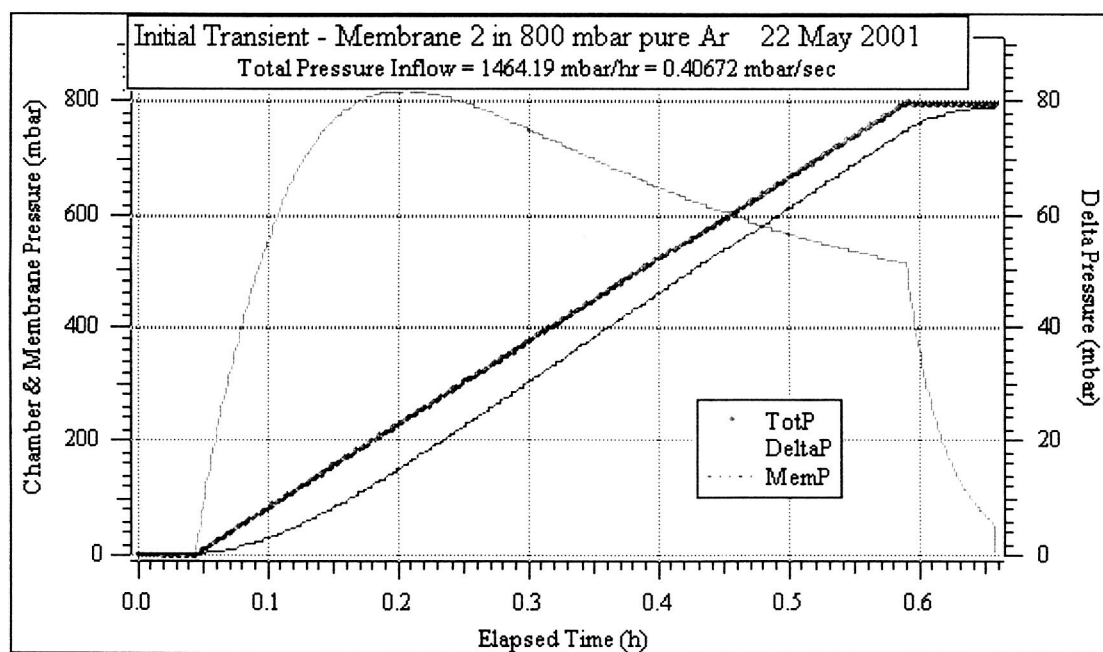


Figure 49 Initial Evaluation of NaY Zeolite Membrane with pure Argon at ambient Temperature

The variation in the delta pressure measurement is caused either by a change in permeance with total pressure, or a leak through the membrane seal. Similar profiles were seen for pure N<sub>2</sub> and CO<sub>2</sub> gases. This may indicate that a leak is present in the membrane seal, because higher total pressure shows a lower delta pressure. A leak in the membrane seal could cause this type of delta pressure profile, because higher total pressure would leak more, and be manifest as a lower delta pressure across the membrane. The membrane seal is currently under investigation as the probable leak path.

Experiments were also conducted using the NaY Zeolite membrane in simulated Mars atmosphere. The tubular configuration was wide open to the chamber, and did not show any evidence of a boundary layer problem. The Mars atmosphere gas mixture contained: 95% CO<sub>2</sub>, 2.8% N<sub>2</sub>, and 1.6% Ar. Table 8 shows a results summary of the NaY zeolite membrane data measured in pure gas experiments. Table 9 shows a results summary of the permeance data measured with Mars gases. Figure 50 shows contour plots of the NaY zeolite membrane permeance as a function of temperature and pressure, in pure gas and Mars atmosphere environments. The NaY zeolite membrane permeance ratios in Mars atmosphere gases are shown in Figure 51.

Table 8 NaY Zeolite Membrane Permeance in Pure Gas (scc/cm<sup>2</sup> s cmHg)

| pure Argon<br>Pres\Temp | -40      | -20      | 0        | 20       | 40       |
|-------------------------|----------|----------|----------|----------|----------|
| 50                      | 2.07E-04 | 2.23E-04 | 2.38E-04 | 2.54E-04 | 2.70E-04 |
| 100                     | 2.20E-04 | 2.34E-04 | 2.48E-04 | 2.62E-04 | 2.76E-04 |
| 250                     | 2.62E-04 | 2.70E-04 | 2.79E-04 | 2.87E-04 | 2.96E-04 |
| 500                     | 3.30E-04 | 3.30E-04 | 3.29E-04 | 3.28E-04 | 3.28E-04 |
| 800                     | 4.13E-04 | 4.01E-04 | 3.89E-04 | 3.78E-04 | 3.66E-04 |

| pure Nitrogen<br>Pres\Temp | -40      | -20      | 0        | 20       | 40       |
|----------------------------|----------|----------|----------|----------|----------|
| 10                         | 3.66E-04 | 3.74E-04 | 3.81E-04 | 3.89E-04 | 3.97E-04 |
| 50                         | 4.24E-04 | 4.35E-04 | 4.46E-04 | 4.57E-04 | 4.68E-04 |
| 100                        | 5.06E-04 | 5.22E-04 | 5.38E-04 | 5.54E-04 | 5.70E-04 |
| 250                        | 7.54E-04 | 7.84E-04 | 8.14E-04 | 8.45E-04 | 8.75E-04 |
| 500                        | 1.17E-03 | 1.22E-03 | 1.27E-03 | 1.33E-03 | 1.38E-03 |
| 800                        | 1.66E-03 | 1.75E-03 | 1.83E-03 | 1.91E-03 | 1.99E-03 |

| pure CO2<br>Pres\Temp | -30      | -20      | 0        | 20       | 40       |
|-----------------------|----------|----------|----------|----------|----------|
| 10                    | 2.30E-04 | 2.47E-04 | 2.93E-04 | 3.38E-04 | 3.52E-04 |
| 50                    | 2.30E-04 | 2.47E-04 | 2.93E-04 | 3.38E-04 | 3.52E-04 |
| 250                   | 2.30E-04 | 2.47E-04 | 2.93E-04 | 3.38E-04 | 3.52E-04 |
| 500                   | 2.65E-04 | 2.80E-04 | 3.16E-04 | 3.52E-04 | 3.63E-04 |
| 800                   | 4.78E-04 | 4.71E-04 | 4.52E-04 | 4.34E-04 | 4.28E-04 |

Table 9 NaY Zeolite Membrane Permeance in Mars Atmosphere (scc/cm<sup>2</sup> s cmHg)

| Mars Ar   |  | -30      | -20      | 0        | 20       | 40       |
|-----------|--|----------|----------|----------|----------|----------|
| Pres\Temp |  |          |          |          |          |          |
| 10        |  | 1.34E-04 | 1.48E-04 | 1.79E-04 | 2.09E-04 | 2.39E-04 |
| 50        |  | 1.50E-04 | 1.64E-04 | 1.94E-04 | 2.24E-04 | 2.54E-04 |
| 100       |  | 1.76E-04 | 1.90E-04 | 2.20E-04 | 2.49E-04 | 2.78E-04 |
| 250       |  | 2.55E-04 | 2.68E-04 | 2.96E-04 | 3.23E-04 | 3.51E-04 |
| 500       |  | 3.86E-04 | 3.97E-04 | 4.22E-04 | 4.47E-04 | 4.71E-04 |

| Mars N2   |  | -30      | -20      | 0        | 20       | 40       |
|-----------|--|----------|----------|----------|----------|----------|
| Pres\Temp |  |          |          |          |          |          |
| 10        |  | 1.70E-04 | 1.87E-04 | 2.22E-04 | 2.57E-04 | 2.92E-04 |
| 50        |  | 1.87E-04 | 2.02E-04 | 2.37E-04 | 2.71E-04 | 3.05E-04 |
| 100       |  | 2.13E-04 | 2.28E-04 | 2.61E-04 | 2.94E-04 | 3.26E-04 |
| 250       |  | 2.92E-04 | 3.05E-04 | 3.34E-04 | 3.62E-04 | 3.90E-04 |
| 500       |  | 4.25E-04 | 4.34E-04 | 4.55E-04 | 4.76E-04 | 4.96E-04 |
| 800       |  | 5.83E-04 | 5.89E-04 | 6.00E-04 | 6.12E-04 | 6.23E-04 |

| Mars CO2  |  | -30      | -20      | 0        | 20       | 40       |
|-----------|--|----------|----------|----------|----------|----------|
| Pres\Temp |  |          |          |          |          |          |
| 10        |  | 2.07E-04 | 1.95E-04 | 1.68E-04 | 1.40E-04 | 1.14E-04 |
| 50        |  | 2.17E-04 | 2.05E-04 | 1.79E-04 | 1.53E-04 | 1.27E-04 |
| 100       |  | 2.32E-04 | 2.21E-04 | 1.96E-04 | 1.72E-04 | 1.49E-04 |
| 250       |  | 2.76E-04 | 2.68E-04 | 2.50E-04 | 2.32E-04 | 2.14E-04 |
| 500       |  | 3.51E-04 | 3.47E-04 | 3.39E-04 | 3.31E-04 | 3.24E-04 |
| 800       |  | 4.41E-04 | 4.43E-04 | 4.47E-04 | 4.51E-04 | 4.54E-04 |

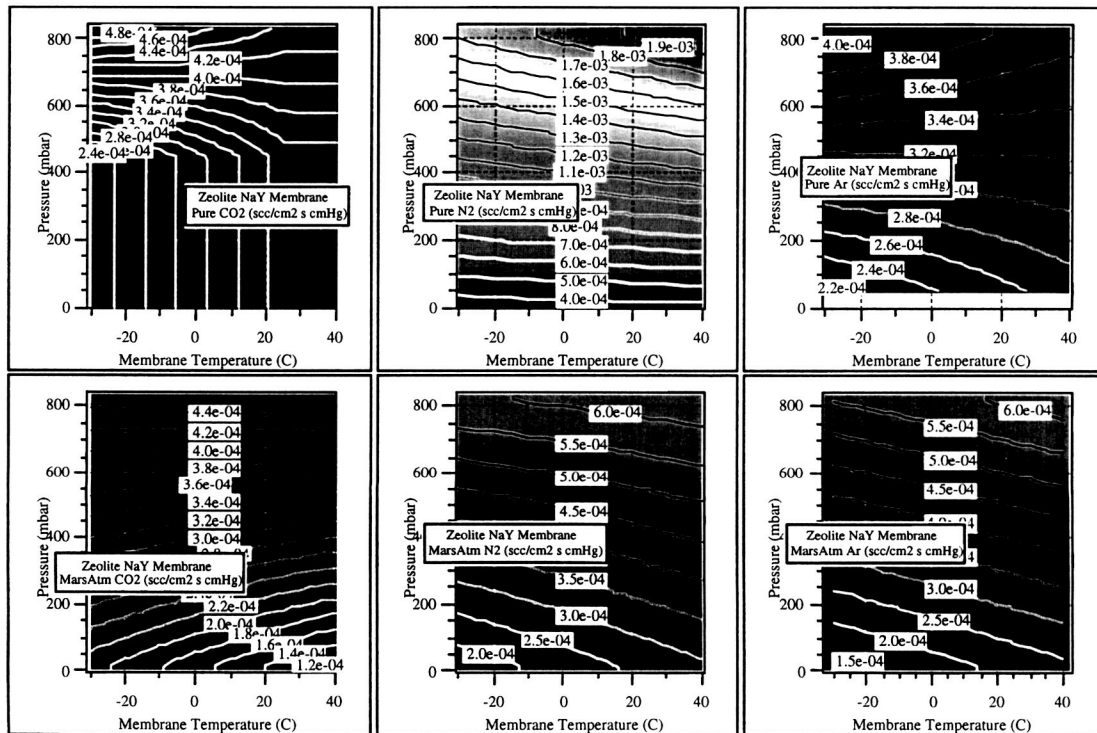


Figure 50 Zeolite Na Membrane Permeance in Pure Gas and Mars Atmosphere

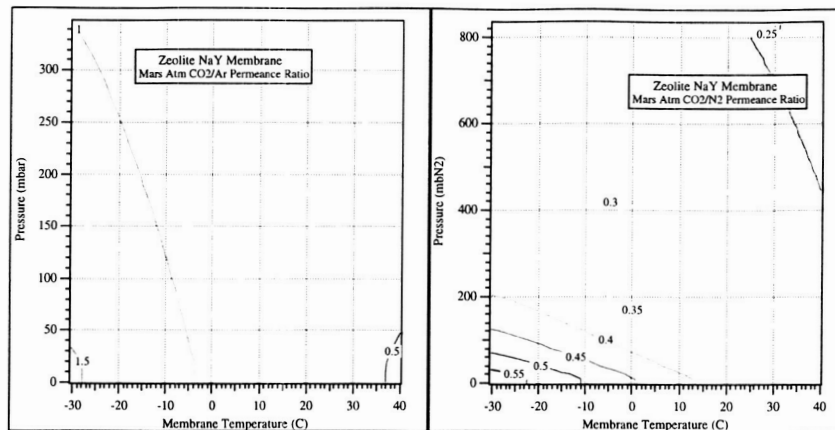


Figure 51 NaY Zeolite Membrane Gas Selectivity in Mars Atmosphere

#### Conclusions from NaY Zeolite Membrane Experiments

This membrane showed higher permeance for N<sub>2</sub> than any other gas, at all temperatures and pressures. The CO<sub>2</sub> / N<sub>2</sub> selectivity was less than one in all tests, with a maximum at low temperature (-30 C) and low pressure (10 mbar), where a permeance ratio of 0.55 was measured (CO<sub>2</sub> / N<sub>2</sub>). The membrane showed marginal selectivity for CO<sub>2</sub> over Ar. The highest permeance ratio measured for these gases was 1.5 (CO<sub>2</sub> / Ar), also at low temperature (-30 C) and low pressure (10 mbar).

#### Zeolite 13 Membrane Characterization in the MTF

A different variety of zeolite membrane was synthesized at CSM, called zeolite 13. This membrane uses a different counterion bound to the zeolite matrix to alter the pore size distribution, and change the gas permeance properties. This thin-film membrane was fabricated on a planar porous alumina support, mounted in the planar membrane holder, and evaluated in the MTF for CO<sub>2</sub>, N<sub>2</sub>, and He permeance. The measured permeance values are shown in Table 10. The membrane shows about the same permeance for both CO<sub>2</sub> and Ar, and shows much less selectivity for He than the original, zeolite 1 membrane. This indicates that the zeolite 13 pore size distribution is quite different than that of the zeolite 1 membrane. However, the selectivity for CO<sub>2</sub> is much less than is desired for Mars ISRU applications.

*Table 10 Zeolite 1 and Zeolite 13 Membrane Permeance Measurements with Pure Gas at Room Temperature*

pure gas permeance [scc/cm<sup>2</sup> sec cmHg]

| <b>Zeolite 1</b> | He       | Ar       | CO <sub>2</sub> | He/Ar | CO <sub>2</sub> /Ar |
|------------------|----------|----------|-----------------|-------|---------------------|
| 800 mbar         | 2.69E-05 | 6.44E-07 | 1.65E-08        | 41.8  | 0.0256              |
| 80 mbar          | 1.47E-05 | 2.63E-06 | 4.37E-08        | 5.6   | 0.0166              |
| 80 mbar          | 1.59E-05 |          |                 |       |                     |

| <b>Zeolite 13</b> | He       | Ar       | CO <sub>2</sub> | He/Ar | CO <sub>2</sub> /Ar |
|-------------------|----------|----------|-----------------|-------|---------------------|
| 800 mbar          | 3.15E-05 | 1.07E-05 | 8.43E-06        | 3.0   | 0.8                 |
| 800 mbar          | 3.20E-05 | 1.09E-05 | 8.54E-06        | 2.9   | 0.8                 |
| 80 mbar           | 3.34E-05 | 8.29E-06 | 8.67E-06        | 4.0   | 1.0                 |
| 80 mbar           | 3.21E-05 |          | 7.97E-06        |       |                     |

#### Poly (ether imide) Copolymer membrane

The first membrane evaluated was a poly (ether imide) copolymer thin film membrane, shown to preferentially remove CO<sub>2</sub> from flue gas [1]. The membrane is comprised of polyethylene oxide (PEO) based copolymers that exhibit high permselectivity for CO<sub>2</sub> over N<sub>2</sub> due to affinity of CO<sub>2</sub> for the PEO segment microdomains.

The measured permeance values for pure gas and Mars atmosphere tests are shown in Table 11 and Table 12. Figure 52 shows the measured pure gas and Mars atmosphere permeance values, and Figure 53 shows the pure gas selectivity.



*Table 11 Poly (ether imide) Copolymer Membrane Permeance In Pure Gas*

| pure Argon |          |          |          |          |          |
|------------|----------|----------|----------|----------|----------|
| Pres\Temp  | -40      | -20      | 0        | 20       | 30       |
| 10         | 8.35E-04 | 7.11E-04 | 5.87E-04 | 4.63E-04 | 4.01E-04 |
| 50         | 1.25E-03 | 1.06E-03 | 8.63E-04 | 6.68E-04 | 5.71E-04 |
| 100        | 1.76E-03 | 1.48E-03 | 1.20E-03 | 9.17E-04 | 7.77E-04 |
| 250        | 3.15E-03 | 2.64E-03 | 2.12E-03 | 1.60E-03 | 1.34E-03 |
| 500        | 5.10E-03 | 4.25E-03 | 3.40E-03 | 2.54E-03 | 2.12E-03 |
| 800        | 6.80E-03 | 5.65E-03 | 4.50E-03 | 3.34E-03 | 2.76E-03 |

| pure Nitrogen |          |          |          |          |          |
|---------------|----------|----------|----------|----------|----------|
| Pres\Temp     | -40      | -20      | 0        | 20       | 30       |
| 30            | 2.15E-03 | 1.58E-03 | 1.02E-03 | 4.54E-04 | 1.72E-04 |
| 50            | 2.10E-03 | 1.57E-03 | 1.03E-03 | 4.99E-04 | 2.32E-04 |
| 100           | 2.02E-03 | 1.55E-03 | 1.08E-03 | 6.07E-04 | 3.72E-04 |
| 250           | 1.96E-03 | 1.60E-03 | 1.24E-03 | 8.77E-04 | 6.98E-04 |
| 500           | 2.53E-03 | 2.07E-03 | 1.61E-03 | 1.15E-03 | 9.24E-04 |
| 800           | 4.34E-03 | 3.29E-03 | 2.25E-03 | 1.20E-03 | 6.74E-04 |

| pure Carbon Dioxide |          |          |          |          |          |
|---------------------|----------|----------|----------|----------|----------|
| Pres\Temp           | -40      | -20      | 0        | 20       | 30       |
| 10                  | 8.19E-04 | 7.37E-04 | 6.22E-04 | 5.07E-04 | 4.49E-04 |
| 50                  | 1.11E-03 | 1.01E-03 | 8.63E-04 | 7.18E-04 | 6.46E-04 |
| 100                 | 1.47E-03 | 1.34E-03 | 1.16E-03 | 9.83E-04 | 8.93E-04 |
| 250                 | 2.56E-03 | 2.36E-03 | 2.07E-03 | 1.78E-03 | 1.63E-03 |
| 500                 | 4.38E-03 | 4.04E-03 | 3.57E-03 | 3.10E-03 | 2.86E-03 |
| 800                 | 6.56E-03 | 6.07E-03 | 5.38E-03 | 4.68E-03 | 4.34E-03 |

*Table 12 Poly (ether imide) Copolymer Membrane Permeance In Mars Atmosphere*

| Mars Argon |          |          |          |          |          |
|------------|----------|----------|----------|----------|----------|
| Pres\Temp  | -30      | -20      | 0        | 20       | 30       |
| 10         | 1.53E-03 | 1.40E-03 | 1.13E-03 | 8.67E-04 | 7.34E-04 |
| 50         | 1.59E-03 | 1.46E-03 | 1.20E-03 | 9.40E-04 | 8.11E-04 |
| 100        | 1.65E-03 | 1.53E-03 | 1.28E-03 | 1.03E-03 | 9.10E-04 |
| 250        | 1.85E-03 | 1.75E-03 | 1.53E-03 | 1.31E-03 | 1.21E-03 |
| 500        | 2.19E-03 | 2.11E-03 | 1.94E-03 | 1.78E-03 | 1.70E-03 |
| 800        | 2.59E-03 | 2.54E-03 | 2.44E-03 | 2.34E-03 | 2.29E-03 |

| Mars Nitrogen |          |          |          |          |          |
|---------------|----------|----------|----------|----------|----------|
| Pres\Temp     | -30      | -20      | 0        | 20       | 30       |
| 10            | 8.82E-04 | 8.32E-04 | 7.34E-04 | 6.35E-04 | 5.86E-04 |
| 50            | 1.27E-03 | 1.19E-03 | 1.05E-03 | 9.06E-04 | 8.34E-04 |
| 100           | 1.72E-03 | 1.63E-03 | 1.44E-03 | 1.25E-03 | 1.16E-03 |
| 250           | 2.87E-03 | 2.76E-03 | 2.54E-03 | 2.32E-03 | 2.21E-03 |
| 500           | 4.07E-03 | 4.10E-03 | 4.14E-03 | 4.19E-03 | 4.21E-03 |
| 800           | 4.33E-03 | 4.78E-03 | 5.68E-03 | 6.57E-03 | 7.02E-03 |

| Mars Carbon Dioxide |          |          |          |          |          |
|---------------------|----------|----------|----------|----------|----------|
| Pres\Temp           | -30      | -20      | 0        | 20       | 30       |
| 10                  | 6.91E-04 | 6.73E-04 | 6.36E-04 | 6.00E-04 | 5.82E-04 |
| 50                  | 9.94E-04 | 9.54E-04 | 8.74E-04 | 7.93E-04 | 7.53E-04 |
| 100                 | 1.38E-03 | 1.31E-03 | 1.17E-03 | 1.04E-03 | 9.69E-04 |
| 250                 | 2.53E-03 | 2.38E-03 | 2.08E-03 | 1.77E-03 | 1.62E-03 |
| 500                 | 4.45E-03 | 4.16E-03 | 3.58E-03 | 2.99E-03 | 2.70E-03 |
| 800                 | 6.76E-03 | 6.30E-03 | 5.38E-03 | 4.46E-03 | 4.00E-03 |

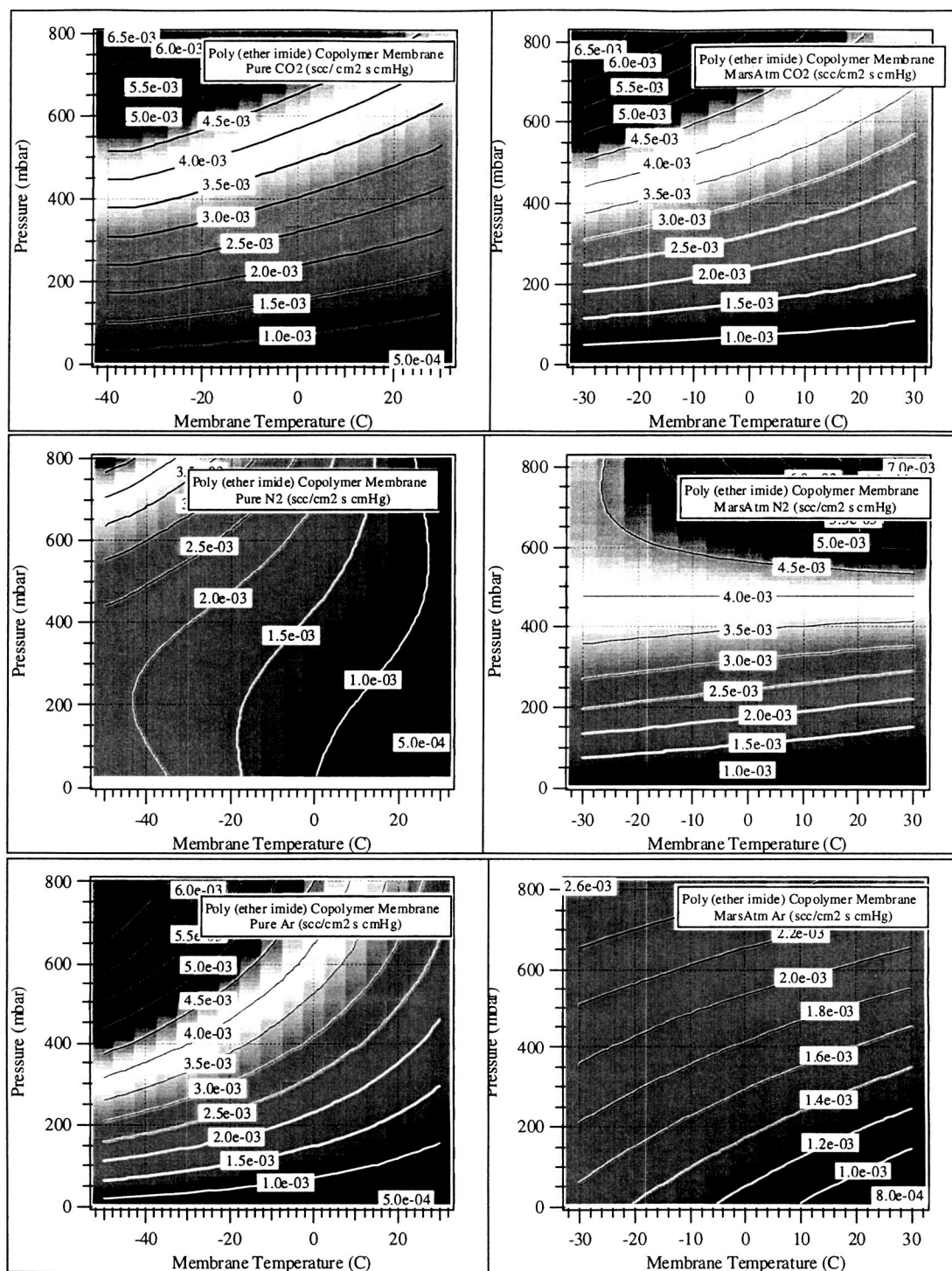


Figure 52 Poly(ether imide) Copolymer Membrane Permeance In Pure Gas and in Mars Atmosphere

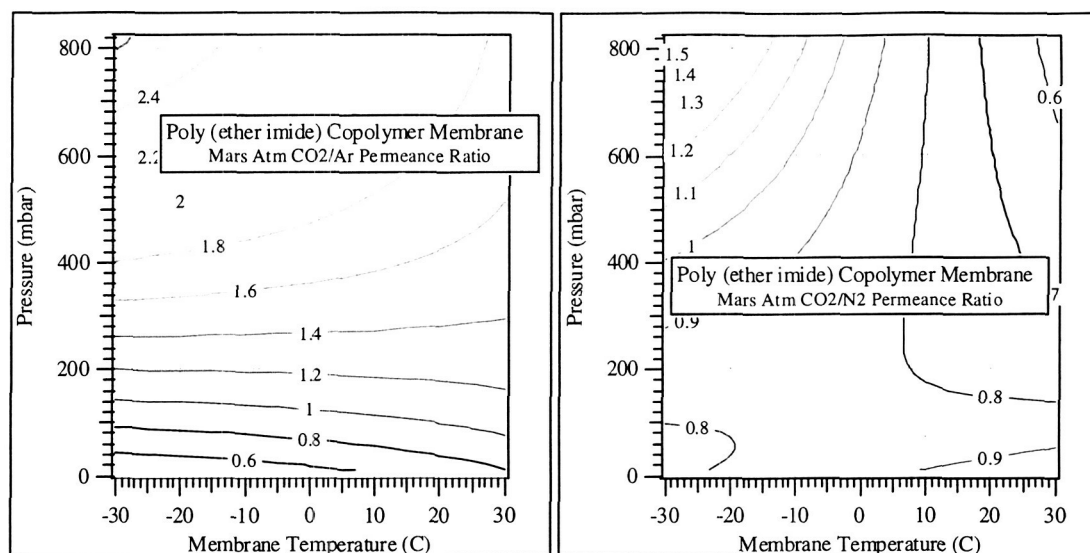


Figure 53 Poly (ether imide) Copolymer Membrane CO<sub>2</sub> Selectivity in Mars Atmosphere

The plots show that the relative membrane pure gas permeance varies as a function of temperature, and pressure. High pressure and low temperature favor CO<sub>2</sub> permeance, and high pressure and high temperature favor N<sub>2</sub> permeance. The selectivity for these gases was determined by dividing the individual gas permeance values as a function of temperature and pressure. The membrane is shown to be moderately selective for CO<sub>2</sub> over both N<sub>2</sub> and Ar under conditions of 800 mbar and -30 deg C.

#### Rubbery Polymer Membranes

A series of related rubbery polymer membranes was tested to determine the effect the relative proportions each constituent polymer showed on gas selectivity. These membranes are relatively thick, and each permeance measurement required several days to perform. For this reason, the membranes were tested using two gases (CO<sub>2</sub> and N<sub>2</sub>), at two pressures (800 mbar and 80 mbar), at room temperature. Figure 54 shows the results of these tests in terms of the relative CO<sub>2</sub>/N<sub>2</sub> gas selectivity as a function of the fraction of constituent polymer materials. Membrane components are specified as a series of three numbers that indicate the relative proportion of each component, for example Rubbery Polymer 442 has 4 parts of component 1, 4 parts component 2, and 2 parts component 3. The polymer blend membranes tested include: 442, 613, 712, 424, and 316.

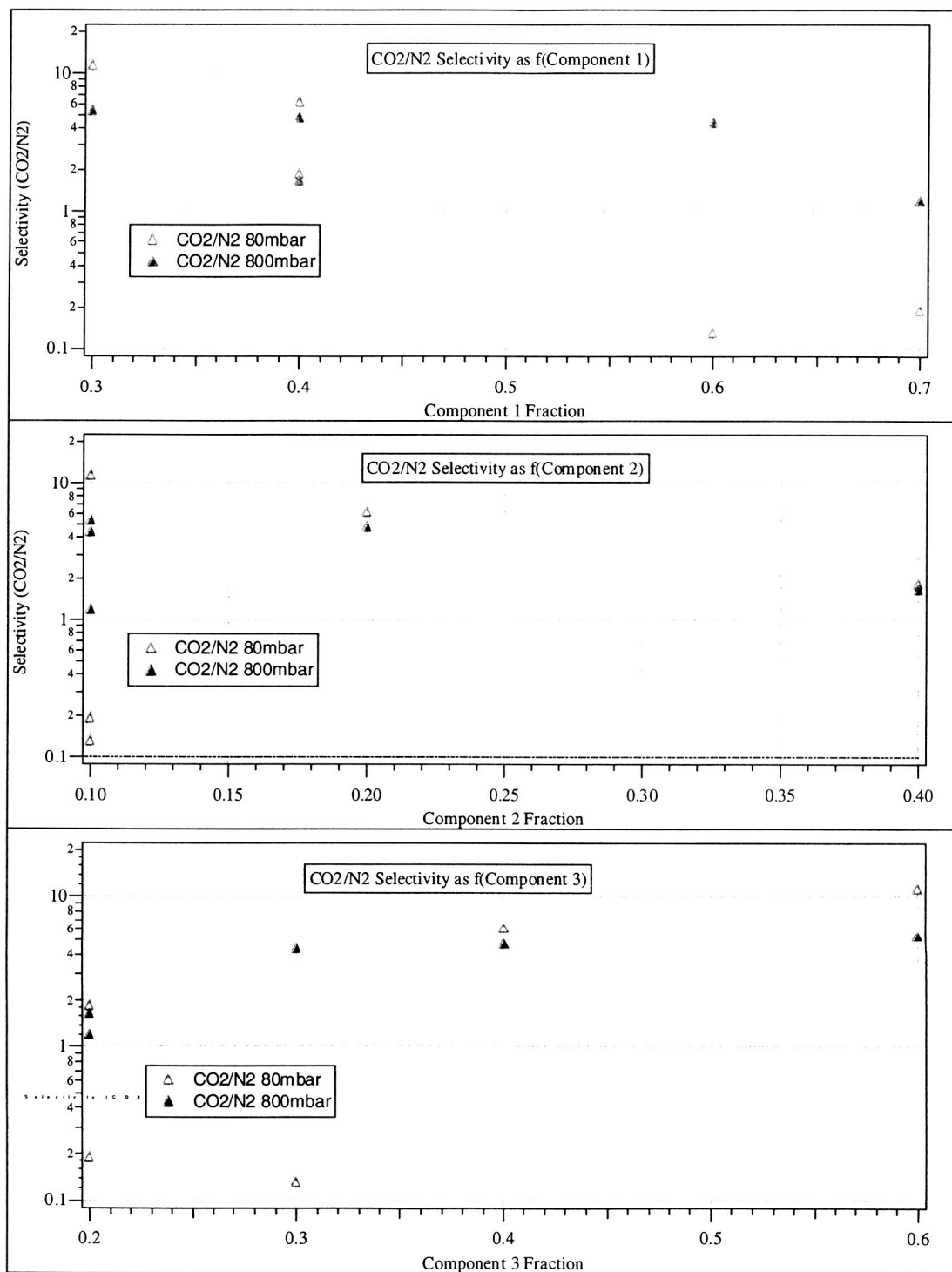


Figure 54 Rubbery Polymer Membrane Selectivity (CO<sub>2</sub>/N<sub>2</sub>) in Mars Atmosphere

### Polyphosphazene Inorganic Polymer Membrane

Polyphosphazenes (PPZ) are inorganic polymers with a backbone consisting of phosphorus and nitrogen (Orme et al., 2001). Properties can be tailored by the choice of the organic pendant group attached to the P=N chain. These polymers have many desirable properties including excellent thermal stability and radiation resistance. PPZ samples used in this work were provided by the membrane group at the Idaho National Engineering and Environmental Laboratory (INEEL). Figure 55 below shows the structure of the PPZ polymer used in this work. Orme and coworkers<sup>1</sup> have shown that the CO<sub>2</sub> permeability of this polymer increases proportionally to the degree of 2-(2-methoxyethoxy)ethanol (MEE) substitution on the P=N backbone. Further, the glass transition temperature decreases as the degree of MEE substitution increases. For the 48% MEE substituted PPZ, the glass transition temperature is 230 K.

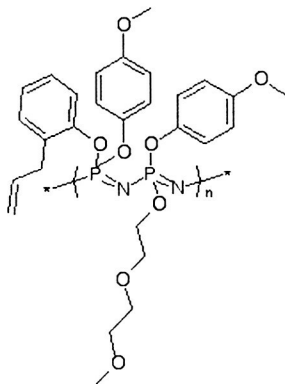


Figure 55. Substituted PPZ used in this work. Our samples have 48% 2-(2-methoxyethoxy)ethanol, 48% 4-methoxyphenol, and 2% 2-allylphenol as a cross-linking agent.

### *Polyphosphazene Membrane Tests in the MTF*

The Polyphosphazene (PPZ) membrane sample obtained from Dr. Orme at INEEL was tested for gas permeance in the MTF. This thin film, inorganic polymer membrane is stable at high temperature, and has been shown to be highly selective for CO<sub>2</sub> over many other gases, including N<sub>2</sub> and Ar. Polyphosphazenes are hybrid polymers that consist of an inorganic backbone composed of phosphorous and nitrogen, with two organic pendant groups attached to each phosphorous. The nature and distribution of the organic pendant groups are thought to provide the gas selectivity through a solution-diffusion mechanism. The relative quantity of various pendant groups can be varied during membrane synthesis, and has been found to significantly affect the physical, chemical, and solubility characteristics of the polymer product. In particular, the organic group 2-(2-methoxyethoxy)ethanol (MEE) provides the polymer product with a polar hydrophilic component. The MEE content in the membrane has shown a positive correlation with CO<sub>2</sub> permeability, thought to occur because of strong intermolecular interactions between

the highly polar CO<sub>2</sub> molecules and the polar MEE pendant groups. Until this time, only room temperature and pressure testing of PPZ membranes had been performed.

The membrane sample is a thin-film supported on an Anopore porous ceramic disk 25 mm in diameter. The membrane is mounted in a stainless steel inline filter holder. Preliminary experiments were performed in the Membrane Test Facility to determine the relative permeance for CO<sub>2</sub>, N<sub>2</sub>, and Ar under standard room and reduced temperature and pressure conditions. The PPZ membrane sample is relatively thick (135 microns), and each gas permeance measurement experiment requires several days to perform. For this reason only a few temperatures and pressures were selected for these preliminary pure gas tests. Figure 56 shows the results of these tests conducted at three temperatures and two pressures.

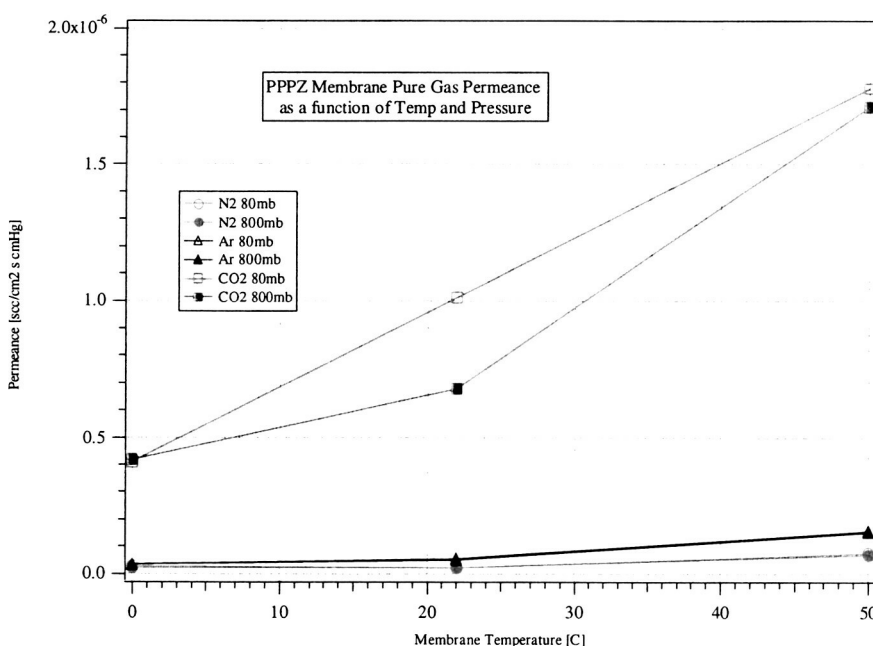


Figure 56 Preliminary Pure Gas PPZ Membrane Permeance Test Results

The selectivity of the membrane for CO<sub>2</sub> over N<sub>2</sub> and Ar was calculated using the preliminary data. Figure 57 shows the results of the selectivity calculations.

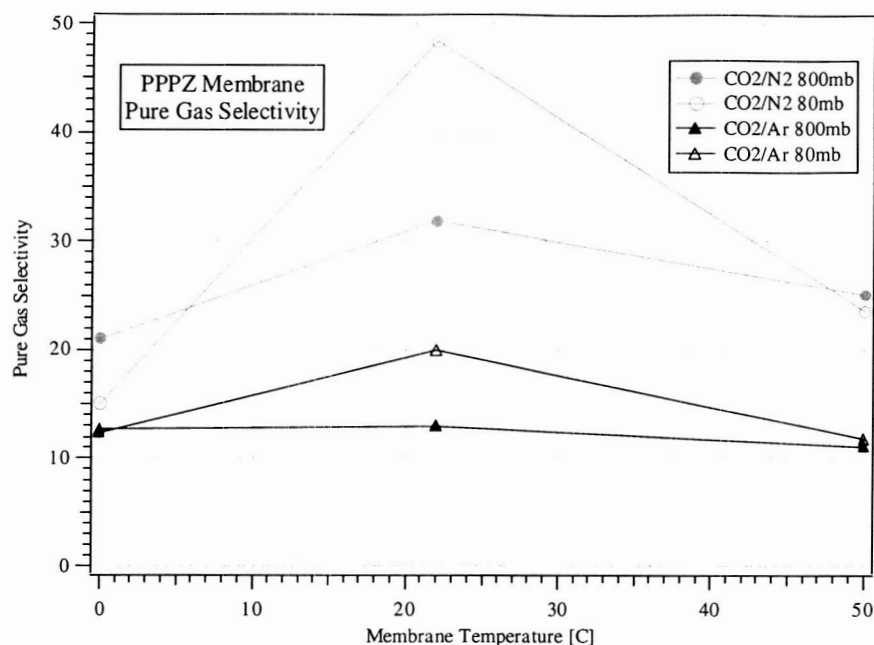


Figure 57 PPZ Membrane Pure Gas Selectivity

These results are very promising, showing that the gas selectivity changes as a function of temperature and pressure, and that there may be a temperature-pressure condition where selectivity is optimum.

A systematic evaluation of the permeance was then performed in this temperature range. The results of the permeance tests are shown in Figure 58, where each data point represents a single permeance measurement under constant temperature and pressure conditions. This membrane was very fragile, and ruptured after the pure gas permeance tests were performed. Unfortunately this occurred before performing tests using simulated Mars atmosphere.

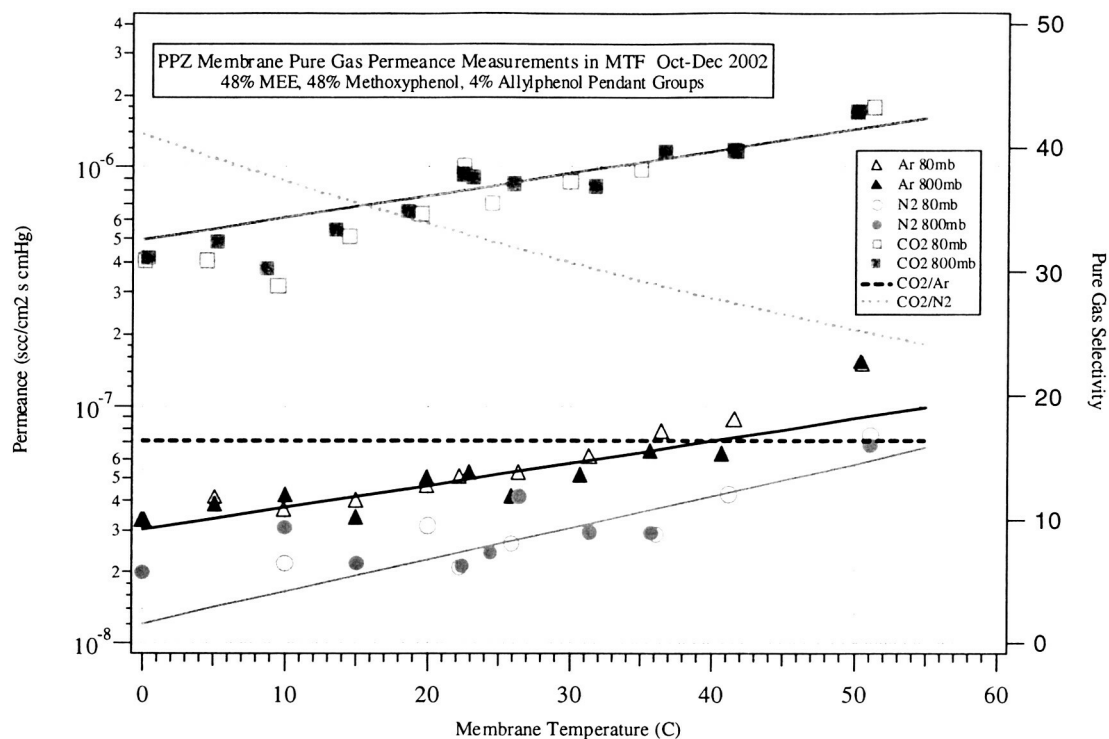


Figure 58 Results from Pure Gas Permeance Measurements on Initial PPZ Membrane Sample from INEEL containing 48% MEE

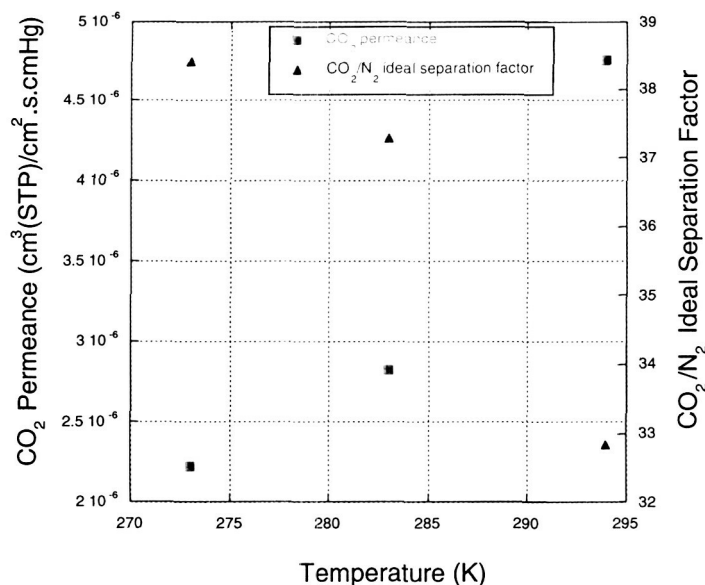
The results show a linear dependence of permeance on temperature, and independence from total pressure. This PPZ membrane copolymer contains 48% MEE as the pendant sidechains on the inorganic phosphazene polymer backbone. Changing the relative percentage of MEE in the copolymer will likely affect the selectivity for CO<sub>2</sub> in the resulting membrane.



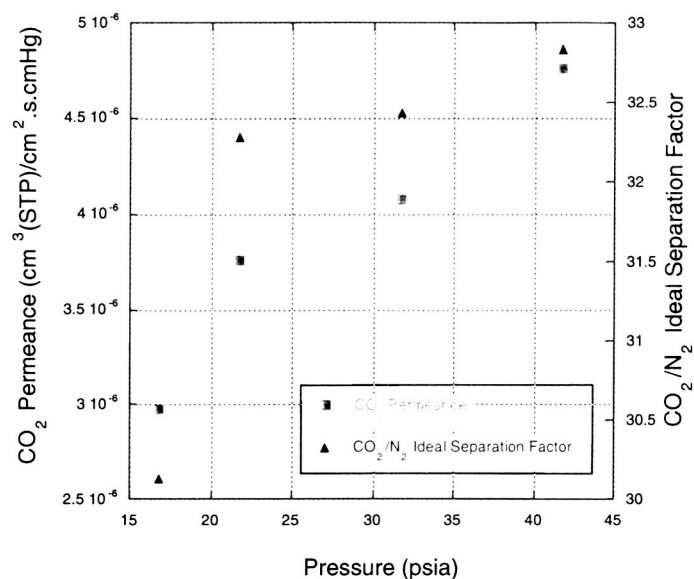
### *PPZ Membrane Fabrication & Test Activities*

The results from the initial PPZ membrane tests in reduced temperature and pressure environments showed high selectivity for CO<sub>2</sub> over both N<sub>2</sub> and Ar gases. These promising results led to a collaborative development of a new version PPZ membrane that has a higher fraction of the pendant group thought to be responsible for the high CO<sub>2</sub> selectivity. The PPZ membranes were fabricated by Dr. Chris Ohme and Dr. Fred Stewart of the Idaho National Engineering and Environmental Lab (INEEL). They have extensive experience and a considerable knowledge base in polymer synthesis and the membrane manufacturing techniques necessary to fabricate these membranes. A small subcontract was initiated with this group to synthesize a batch of polymer having 74% MEE content, much higher than the previous sample. INEEL also performed the membrane casting, and produced several membranes of about 10 microns thickness, supported on a porous stainless steel screen.

Preliminary testing of these membranes was accomplished at atmospheric pressure to measure the dependence of pure gas permeance on temperature. Figure 59 and 60 show the results of these tests, and show the measured selectivities for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/Ar.



*Figure 59 PPZ Membrane Pure Gas Permeance Tests to Measure the Effect of Temperature on CO<sub>2</sub>/N<sub>2</sub> Selectivity*



*Figure 60 PPZ Membrane Pure Gas Permeance Tests to Measure the Effect of Pressure on CO<sub>2</sub>/N<sub>2</sub> Selectivity*

The new PPZ membrane polymer was also tested in the MTF to measure the pure gas permeance at several temperatures and pressures, with the permeance results shown in Figure 61 and the gas selectivity ratios shown in Figure 62. The thinner membrane showed much higher permeance for all gases than the previous, thicker membrane. For this reason the new membranes required much less time to test, about one hour per measurement. However, the gas selectivity was significantly reduced compared to the 48% MEE membrane.

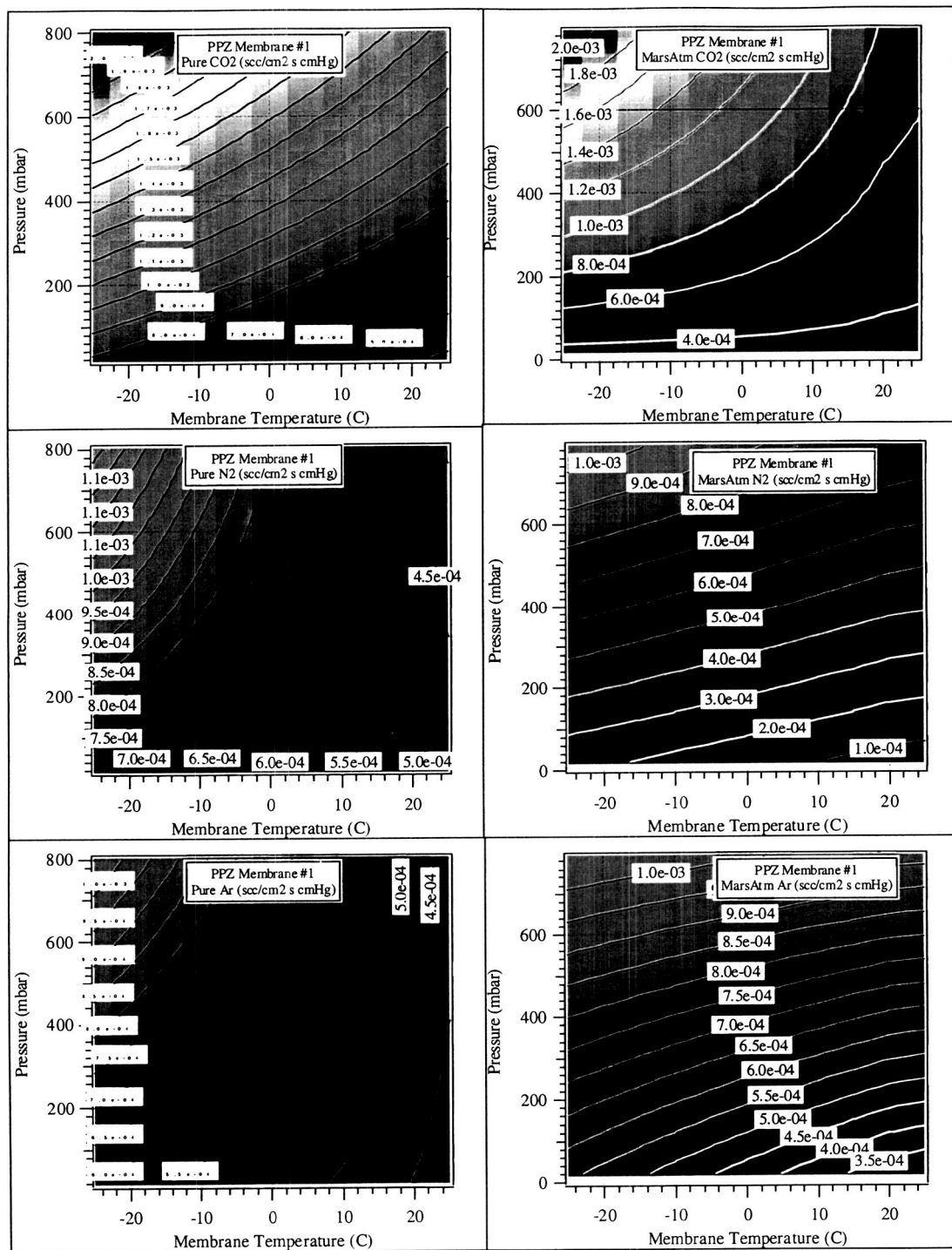


Figure 61 PPZ Membrane Preliminary Test Results with 74% MEE Copolymer

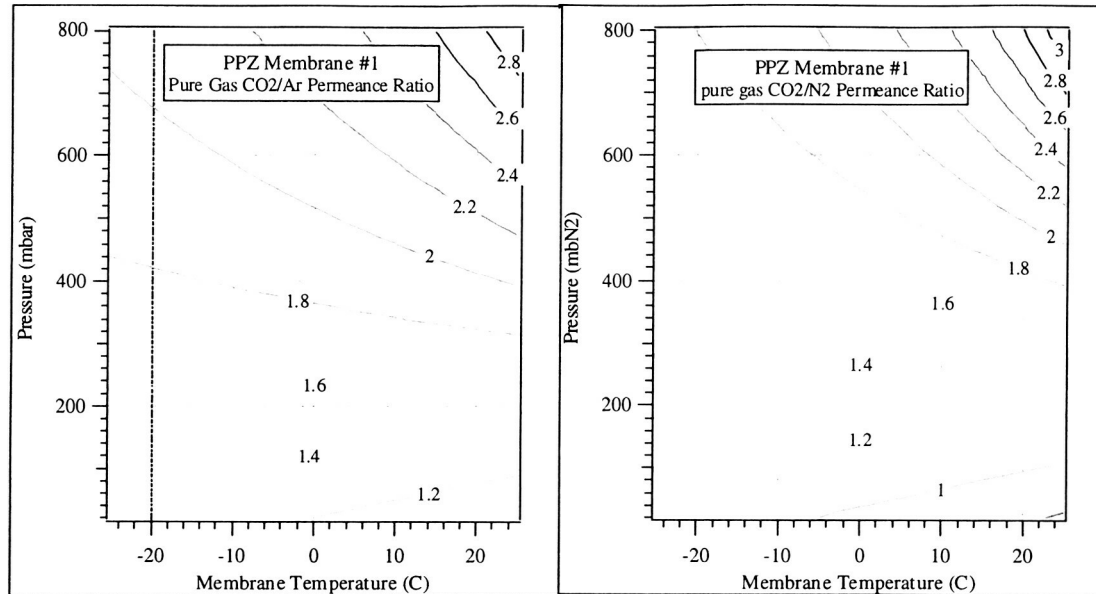
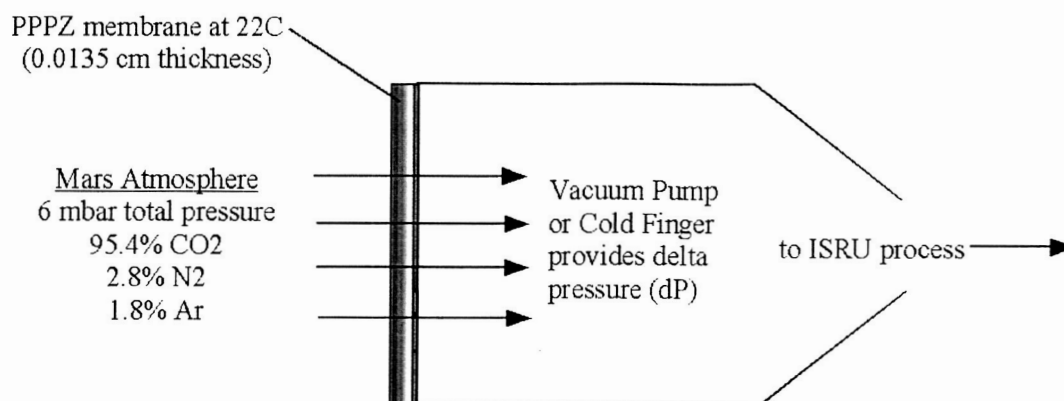


Figure 62 PPZ Membrane Pure Gas CO<sub>2</sub> Selectivity

Published results from PPZ membranes with similar composition [Orme, 2001] show a much higher CO<sub>2</sub> selectivity. The measured gas permeations for the PPZ membrane with 48% MEE were independent of total pressure, and showed a trend of increasing CO<sub>2</sub>/N<sub>2</sub> selectivity with decreasing temperature. This is ideal for use on Mars where low total pressure and low temperature define the environment. The PPZ membrane fabricated with 74% MEE content shows much higher permeance, but significantly reduced selectivity for CO<sub>2</sub>. This membrane also showed a significant total pressure dependence that was absent in the 48% MEE membrane. This information leads to the conclusion that the membranes used in our tests were not completely sealed, and a leak was responsible for the pressure dependence and decreased CO<sub>2</sub> selectivity. Additional testing of these promising membranes is planned for future activities.

#### *PPZ Membrane Application to Mars ISRU*

The PPZ membrane test results show that reduced temperature results in increased selectivity for CO<sub>2</sub>. These test results were used to predict how a PPZ membrane may function in an ISRU application on Mars. Figure 63 shows the schematic of a front-end CO<sub>2</sub> acquisition system for an ISRU process that where atmospheric CO<sub>2</sub> passes through a PPZ membrane, and is enriched in preparation for use. In this case, a vacuum pump or cold finger provides the driving force for transport of CO<sub>2</sub> through the membrane.



*Figure 63 Schematic Diagram of a CO<sub>2</sub> Acquisition System Front End Using a PPZ Membrane*

The gas stream produced by passing Mars atmosphere gas through the membranes was calculated using permeance values for the PPZ membrane measured in the MTF at 80 mbar total pressure and 22 C, where the selectivities were measured to be CO<sub>2</sub>/N<sub>2</sub> = 48, and CO<sub>2</sub>/Ar = 32. Table 13 shows the results of these calculations, indicating that the permeate stream is dramatically enriched in CO<sub>2</sub>. Figure 64 shows the results of this calculation in terms of the predicted flow of CO<sub>2</sub>, N<sub>2</sub>, and Ar as a function of membrane area.

*Table 13 Predicted Gas Composition of Feed and Permeate Streams for PPZ Membrane in ISRU CO<sub>2</sub> Enrichment Application*

|                                          | Carbon<br>Dioxide | Nitrogen | Argon |
|------------------------------------------|-------------------|----------|-------|
| Mars Atmosphere<br>(feed stream)         | 95                | 2.8      | 1.8   |
| Membrane<br>Permeate (product<br>stream) | 99.8              | 0.064    | 0.094 |

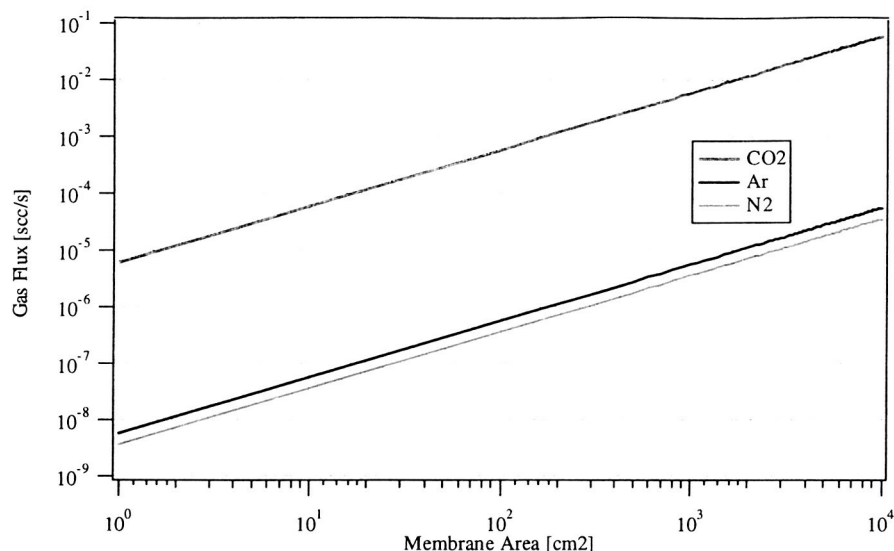


Figure 64 Predicted PPZ Membrane Gas Flow and Composition for CO<sub>2</sub> Enrichment in Preparation for ISRU Application

Membrane permeance is affected by several factors, including the temperature and pressure environment. The flow kinetics are dictated by the membrane thickness. Additional activities are required to determine the utility of the membrane for use with a variety of ISRU processes and applications such as Sabatier reaction systems, Reverse Water Gas Shift reactions, and Environmentally Closed Life Support Systems. In addition, the relative sensitivity of the various parameters on gas selectivity and flow properties must be determined, including tests with mixed gases (Mars and Earth atmospheres), measurement of O<sub>2</sub> and CO permeance, and determination of the permeance characteristics of thinner membranes. These activities will lay the foundation to develop membranes that are optimized for use in ISRU applications on Mars.

#### Ionic Liquid Membrane

Initial CO<sub>2</sub> and N<sub>2</sub> transport experiments have begun using a room temperature supported ionic liquid membrane (SILM). These data are plotted in Figure 61. The ionic liquid selected for this experiment was 1-butyl-3-methylimidazolium phosphorous hexafluoride ([bmim][PF<sub>6</sub>]). Room temperature ionic liquids are molten salts that are liquid at room temperatures. They generally have properties that are more conducive to industrial application than higher melting salts. They are generally believed to have zero vapor pressure, making them more attractive for membrane applications than traditional liquid membranes, which may evaporate away if used in a continuously operating process. An 80 μm thick cellulose filter (Millipore) was used to support the ionic liquid membrane. Permeation studies were performed as a function of temperature using a He stream to sweep the permeating gas away from the membrane, and a gas chromatograph to measure the concentration of the permeate gas. The feed pressure was 17 psia = 1170 mbar.

It is clear from the data obtained that carbon dioxide permeates preferentially over nitrogen. In our initial measurements, we have had trouble quantitating the selectivity as the nitrogen permeance was low enough to test the limits of the detection equipment. The data plotted in Figure 65 represents the upper limit of nitrogen permeance.

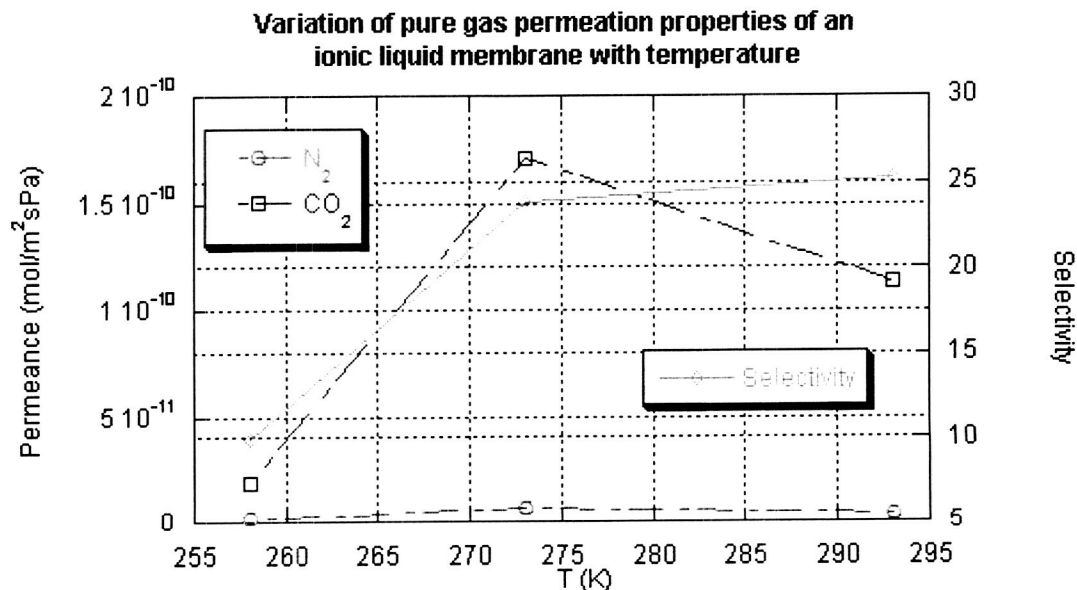
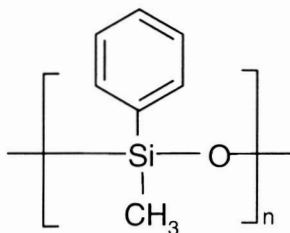


Figure 65. Preliminary pure gas carbon dioxide and nitrogen permeance through a cellulose film supported [bmim][PF6] ionic liquid membrane. Nitrogen permeance represents the upper threshold of accurate detection, and actual nitrogen permeance is likely smaller.

The actual nitrogen permeation is likely smaller than this, and therefore the selectivity will be higher. Carbon dioxide / nitrogen pure gas selectivities of 30 at room temperature have been reported for this same ionic liquid in a polyethylsulfone filter support (Scovazzo et al., 2001). The selectivities of this membrane are likely in the same range. Further studies will be done once the detection equipment is improved to obtain a more accurate measure of nitrogen permeance. Additionally, it was observed that the permeation behavior of the SILM displayed hysteresis if the temperature was raised above 20° C. The observed selectivity would decrease below its initial value if the temperature was raised above 20° C and then returned to the original temperature. It is unclear if this is due to changes in the ionic liquid or in the cellulose support. When permeation was measured at 90° C, the membrane failed after a period of 10 hours. Again, it is unclear if this is due to the support weakening at these higher temperatures or due to the ionic liquid vaporizing.

#### Poly Methyl-Phenyl Siloxane (PMPS) Membrane

This siloxane polymer was obtained from Dow Corning, product no. 3-6121 low temperature silicone elastomer. FTIR-ATR spectroscopy was done on the polymer and the major component was found to be poly(methylphenylsiloxane), shown in Figure 66. The other possible components are dimethyl, methylhydrogen siloxane.



*Figure 66 Structure of poly(methylphenylsiloxane)*

A thermal analysis experiment was done to measure the glass transition temperature of the polymer and it was found to be -45 oC. This value is typical of the temperatures encountered on the Martian surface, and thus the polymer would remain in the rubbery state that enables it to have enhanced permeances over other glassy polymers that are below the glass transition temperature. A casting procedure was developed to make a membrane film of 30-40 microns nominal thickness.

Pure gas permeation tests with CO<sub>2</sub>, N<sub>2</sub>, Ar were performed with the PMPS membrane over a temperature range -10C to 21C at a differential pressure of 20 psi (1360 mbar). The measurements were made under the steady state conditions and the volumetric flow rate on the permeate side was measured by a bubble flowmeter. Figure 67 shows the variation of the CO<sub>2</sub> permeance and the CO<sub>2</sub>/N<sub>2</sub> ideal separation factor as a function of temperature, and Figure 68 shows the pressure effects.



The CO<sub>2</sub> permeance shows an increase with lowering the temperature due to an increase in the CO<sub>2</sub> solubility in the polymer. Whereas, both N<sub>2</sub> and Ar show a decreasing trend in permeance as temperature decreases which can be attributed to the fact that the gases are non-interacting and very less soluble in polymer (solubility values in Table 14) and thus with decreasing the temperature, the permeance decreases due to the decrease in diffusion coefficient.

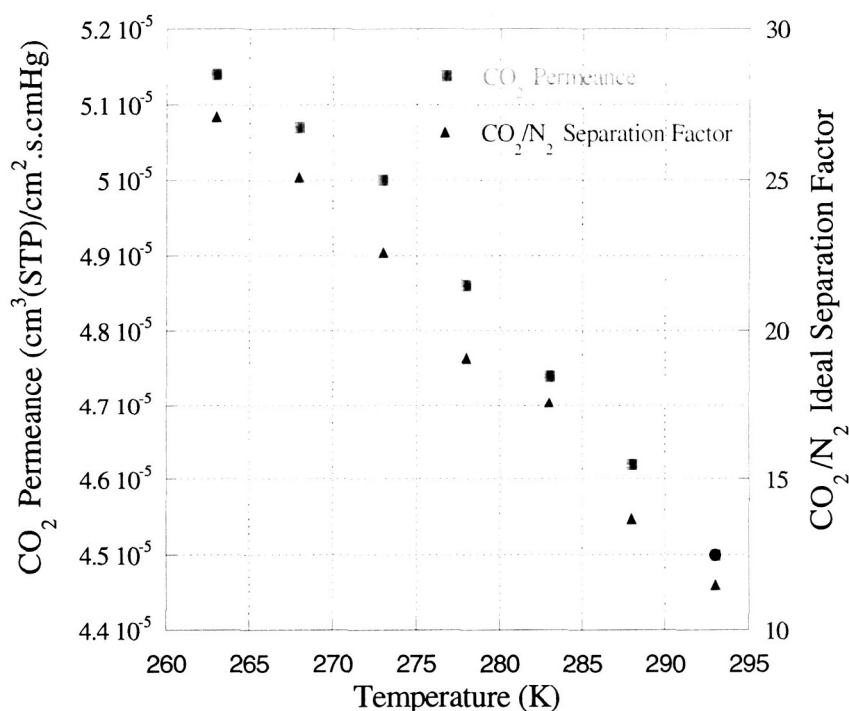


Figure 67 Effect of temperature on CO<sub>2</sub>/N<sub>2</sub> ideal separation factor. Permeation tests conducted at a differential pressure of 20 psi and membrane thickness being 32 μm<sup>1</sup>

<sup>1</sup> Permeability (Barrers)=10<sup>10</sup> x permeance(cm<sup>3</sup>/s.cm<sup>2</sup>.cmHg) x membrane thickness (cm)

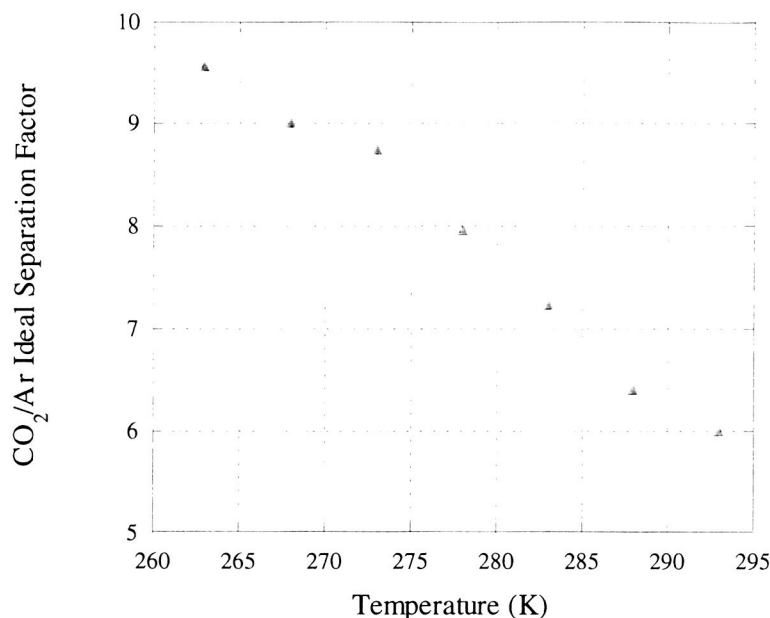


Figure 68 : Effect of temperature on CO<sub>2</sub>/Ar ideal separation factor. Permeation tests conducted at a differential pressure of 20 psi and membrane thickness being 32  $\mu\text{m}$ .

In the case of CO<sub>2</sub>, the increase in solubility with decreasing temperature is greater than the effect of the decrease in diffusion coefficient, thus the permeance increases.

Transient (time lag) permeation experiments were also conducted with PMPS at atmospheric pressure and room temperature that gave the solubility and diffusion coefficient values for the gases. The solubility of CO<sub>2</sub> in the polymer was found to be two magnitudes higher than N<sub>2</sub>.

Table 14 Solubility and Diffusion Coefficient data at atmospheric feed pressure and room temperature.

| Gas             | Permeance<br>(cm <sup>3</sup> /s.cm <sup>2</sup> .cmHg)<br>(Membrane thickness:280 $\mu\text{m}$ ) | Solubility              | Diffusion<br>Coefficient (cm <sup>2</sup> /s) |
|-----------------|----------------------------------------------------------------------------------------------------|-------------------------|-----------------------------------------------|
| CO <sub>2</sub> | 4.97*10 <sup>-6</sup>                                                                              | 1.698 *10 <sup>-2</sup> | 8.2 * 10 <sup>-6</sup>                        |
| N <sub>2</sub>  | 3.9*10 <sup>-7</sup>                                                                               | 2.064 *10 <sup>-5</sup> | 5.38*10 <sup>-4</sup>                         |
| Ar              | 9.4*10 <sup>-7</sup>                                                                               | 2.08 * 10 <sup>-3</sup> | 1.18*10 <sup>-5</sup>                         |

The permeability of CO<sub>2</sub> for the PMPS membrane determined under the steady state conditions is 1440 Barrers and the value from the transient (time lag) permeation test is 1392 Barrers, both tests being done at room temperature. The permeability values of CO<sub>2</sub> from two different methods are within 5% of each other and thus are in good agreement with each other.

Preliminary mixed gas permeation studies with PMPS were also conducted with a binary feed mixture containing 95 %  $\text{CO}_2$  and 5 %  $\text{N}_2$  with feed pressure of 21.8 psia (1482 mbar) at room temperature. A helium sweep was used to move the permeating gases out of the cell and carry them to the gas chromatograph for analysis. The  $\text{CO}_2$  mixed gas permeability decreased by approximately 20% compared to the pure gas value. However, the  $\text{CO}_2/\text{N}_2$  mixture separation factor was 12.9, slightly higher than the pure gas separation factor. The drop in  $\text{CO}_2$  permeability could be due to competitive absorption in the polymer material. More extensive experiments for mixed gas permeation studies need to be performed with different feed compositions and temperatures.

#### *PMPS Membrane Tests in the MTF*

A sample of the PMPS membrane was tested in the MTF under reduced pressure and temperature conditions to determine the  $\text{CO}_2$  permeance relative to  $\text{N}_2$  and Ar. Figure 69 shows the pure gas permeance measurement results, and Figure 70 shows the ideal selectivities for  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{Ar}$ .

This membrane shows very high permeance for  $\text{CO}_2$ , and relatively low permeance for both  $\text{N}_2$  and Ar. The  $\text{CO}_2$  permeance is a function of both temperature and pressure, permeance increases with both temperature and pressure.  $\text{N}_2$  and Ar permeance are mostly independent of pressure, but both gases show a strong temperature dependence. This difference in permeance characteristics suggests that differences in solubility may be responsible for the observed  $\text{CO}_2$  selectivity.

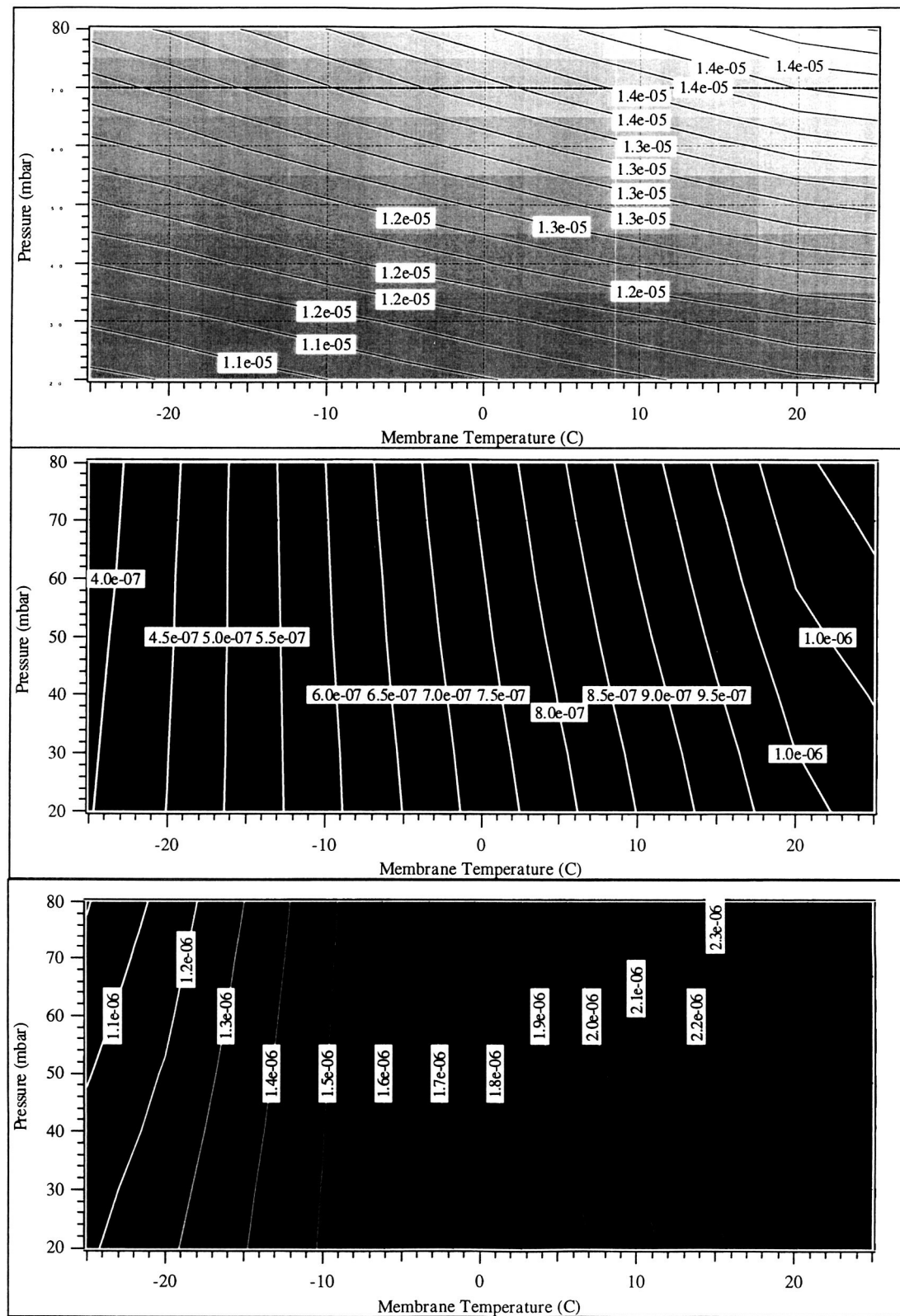


Figure 69 PMPS Membrane Pure Gas Permeance

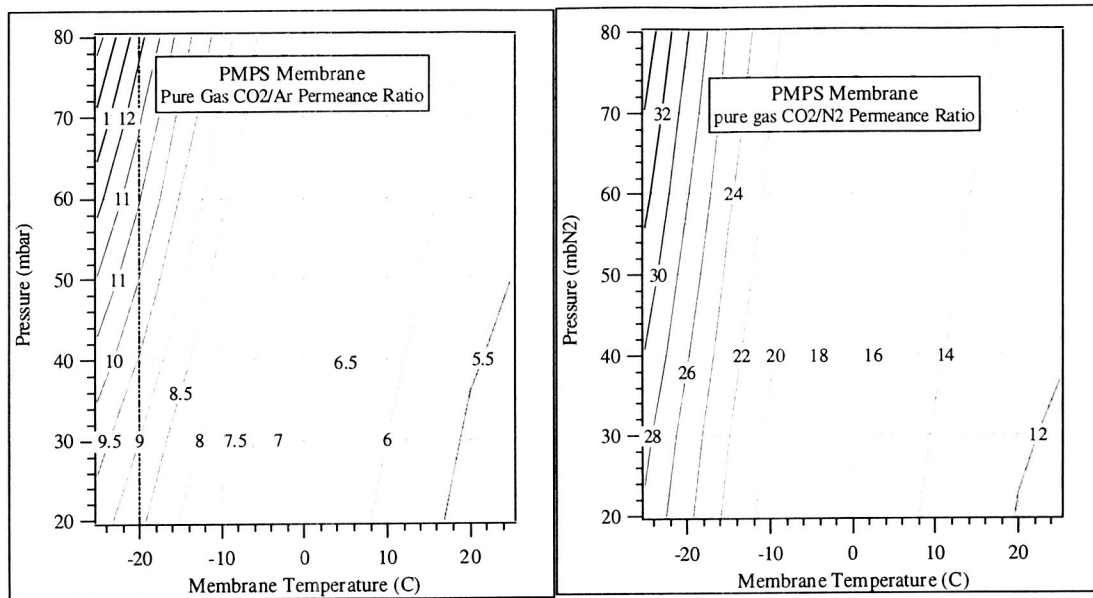


Figure 70 PMPS Membrane Ideal CO<sub>2</sub> Selectivity

### Other CAM Project Progress

Prof. Way presented a paper, # IAC-02-IAA.13.3.06, describing project data using results from the silicone rubber (PDMS) and polyphosphazene membranes at the October 2002 World Space Congress meeting in Houston, TX. The paper was presented in a session dealing with a range of ISRU technologies. The manuscript can be found in the Appendix to this report.

### CAM Project Summary, Conclusions, & Recommendations

The CAM program was performed to develop, test, and analyze membrane materials for separation and purification of carbon dioxide from mixtures of gases such as those found in the Martian atmosphere. The membranes developed and identified over the course of the CAM program will be used in future missions to Mars in conjunction with *In Situ Resource Utilization* systems to acquire and utilize carbon dioxide and trace gases from the Mars atmosphere. The purified gases acquired using CAM membranes will be used in systems that produce methane, oxygen, and water for fuel and life support. In this way the CAM program represents enabling technology for autonomous and manned surface operations that will support exploration of the red planet.

Significant technology advancements were achieved during the CAM program. The Membrane Test Facility was developed to measure gas permeance of candidate membranes over a wide range of temperatures and pressures. Novel techniques were developed to measure gas permeance, and to analyze the data in the context of ISRU

applications. The MTF was used to evaluate the candidate membranes in terms of pure gas permeance, and gas separation performance in a simulated Mars atmosphere environment.

A range of membrane materials were identified as candidates for CAM research. The materials investigated include: silicone rubber and silicone derivatives, several forms of zeolite-based microporous materials, inorganic polymeric materials with varying organic pendant side chains, a variety of rubbery polymers, and poly ether imide copolymers. These materials were identified as candidates based on material properties such as gas solubility and diffusion, glassy transition temperature, and published permeability data acquired at atmospheric pressure. Table 15 summarizes the measurement results for membrane type sorted by the  $\text{CO}_2/\text{N}_2$  selectivity, and also lists the optimal temperature & pressure, and measured  $\text{CO}_2$  permeance.

*Table 15 Summary of Membrane  $\text{CO}_2$  Permeance and Selectivity*

| Membrane         | $\text{CO}_2$ Permeance<br>[scc cm <sup>2</sup> s cmHg] | $\text{CO}_2/\text{N}_2$ Selectivity<br>[P- $\text{CO}_2$ /P- $\text{N}_2$ ] | $\text{CO}_2/\text{Ar}$ Selectivity<br>[P- $\text{CO}_2$ /P-Ar] | Temperature<br>[C] | Pressure<br>[mbar] |
|------------------|---------------------------------------------------------|------------------------------------------------------------------------------|-----------------------------------------------------------------|--------------------|--------------------|
| PPZ 48% MEE      | 5.0E-06                                                 | 40                                                                           | 16                                                              | 0                  | P independent      |
| PPZ 74% MEE      | 1.3E-03                                                 | 38                                                                           | -                                                               | 25                 | 2750               |
| PMPS             | 1.3E-05                                                 | 34                                                                           | 13                                                              | -25                | 80                 |
| PF6 Ionic Liquid | 2.0E-10                                                 | 25                                                                           | -                                                               | 5                  | 830                |
| PDMS             | 6.0E-04                                                 | 4                                                                            | 4                                                               | -25                | 800                |
| PEI copolymer    | 6.5E-03                                                 | 2.63                                                                         | 1.5                                                             | -30                | 800                |
| Zeolite NaY      | 2.4E-04                                                 | 1.5                                                                          | 0.55                                                            | -25                | 20                 |
| Zeolite 13       | 8.7E-06                                                 | 1.5                                                                          | 0.55                                                            | -25                | 20                 |
| Zeolite 1        | 2.7E-05                                                 | -                                                                            | 0.03                                                            | 25                 | 800                |

The inorganic polymer PPZ membrane shows very promising separation characteristics that may be further optimized for the Mars environment. Additional tests are required to determine the effect of membrane thickness on the gas selectivity and permeance. The PMPS membrane has a very low glassy transition temperature, and also shows respectable gas separation characteristics for use on Mars. Additional testing of this material is also warranted to optimize the gas selectivity and to determine the effects of other environmental influences such as radiation. Further, packaging and support structures for the delicate thin-film membrane must be designed and tested to endure the rigors of space-flight. These activities will increase the Technology Readiness Level (TRL) of membrane assemblies to the point where they can realistically be considered for use on a mission to Mars.

These results show that the CAM program has identified membrane materials to effect significant separation of  $\text{CO}_2$  from Mars atmospheric gases. Ideal gas separation factors were measured up to 40 for  $\text{CO}_2/\text{N}_2$  and 16 for  $\text{CO}_2/\text{Ar}$ , enabling a “front-end” filter/membrane assembly that will function to concentrate  $\text{CO}_2$  directly from the Mars atmosphere. Alternate configuration using the same filter/membrane element can be used to concentrate  $\text{N}_2$  and Ar trace gases.

## REFERENCES

- Kumakiri, I., "Preparation and Permeation-Mechanism of Zeolite Membranes, "Ph.D. Dissertation, Dept. of Chemical Systems Engineering, University of Tokyo, Tokyo, Japan, 2000.
- Kusakabe, K., Kuroda, T., Murata, A., and S. Morooka, *Ind. Eng. Chem. Res.*, **36**, 649(1997).
- Kusakabe, K., Kuroda, T., and S. Morooka, *J. Membr. Sci.*, **148**, 13(1998b).
- Kusakabe, K., Gohgi, S., and S. Morooka, *Ind. Eng. Chem. Res.*, **37**, 4262(1998a).
- Okamoto, K., M. Fujii, S. Okamoto, H. Suzuki, K. Tanaka, and H. Kita, *Macromolecules*, **28**: 6950 (1995).
- Orme, C. J., Harrup, M. K., Luther, T. A., Lash, R. P., Houston, K. S., Weinkauf, D. H., and F. F. Stewart, Characterization of Gas Transport in Selected Rubbery Amorphous Polyphosphazene Membranes," *J. Membr. Sci.*, **186**, 249-256(2001).
- Robb, W. L., "Thin silicone membranes-Their permeation properties and some applications," *Annals New York Academy of Sciences*, **146**, 119(1968).
- Scovazzo, P., Visser, Ann, Davis, James, Rogers, Robin, Koval, Carl, DuBois, Dan, and Noble, Richard (2001). Supported Ionic Liquid Membranes (SILMs) and Facilitated Ionic Liquid Membranes (FILMs). In Industrial Applications of Ionic Liquids. American Chemical Society, Editors: R. A. Rogers, K. R. Seddon.

## APPENDIX –

Paper submitted to World Space Congress Meeting, Houston, TX October 2002

## MARTIAN AIR SEPARATION FOR IN-SITU RESOURCE UTILIZATION PROCESSES

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**Abstract** The concept of using synthetic membranes for the separation and purification of carbon dioxide (CO<sub>2</sub>) from the Martian atmosphere for *In-Situ Resource Utilization (ISRU)* is introduced. ISRU involves the use of resources present on Mars, to reduce the amount of material that must be transferred from Earth. Pure gas and mixed gas permeation tests with CO<sub>2</sub>, Ar, N<sub>2</sub>, and O<sub>2</sub> were performed over the temperature range 243 K to 295 K with a several candidate membrane materials including rubbery polymers (silicone rubber and substituted polyphosphazenes). In experiments with commercially available silicone rubber membranes, the pure gas CO<sub>2</sub> permeance (flux/driving force) increases from 460 GPU to 655 GPU as the temperature decreases from 295 K to 243 K. A GPU is a commonly used unit of permeance and is defined as 10<sup>-6</sup> cm<sup>3</sup>(STP)/cm<sup>2</sup>•s•cm Hg. The ideal carbon dioxide/nitrogen separation factor (ratio of pure gas permeances) increases from 7.5 to 17.5 over the same temperature range. However, in mixed gas experiments, the CO<sub>2</sub>/N<sub>2</sub> separation factor was much lower, increasing from 4.5 to 6 as the temperature decreased from 295 K to 243 K. Preliminary permeability data for CO<sub>2</sub>, N<sub>2</sub>, and Ar for a polar polyphosphazene polymer were measured at 295 K. For a feed pressure of 80 mbar, the CO<sub>2</sub> permeability

was 137 Barrer and the CO<sub>2</sub>/N<sub>2</sub> ideal separation factor was 48.5.

### INTRODUCTION

This paper will describe the use of synthetic membranes for the separation and purification of carbon dioxide (CO<sub>2</sub>) from mixtures of gases, such as those found in the Martian atmosphere. CSM and Lockheed Martin are collaborating to develop membranes to passively separate these gases, enable energy efficient acquisition and purification of these important resources, and lay the foundation for future unmanned sample return and human space missions. The membranes developed in this project are targeted toward *In Situ Resource Utilization (ISRU)* applications, such as *In Situ Propellant Production (ISPP)* and *In Situ Consumables Production (ISCP)*. The membrane materials could potentially be located at the atmospheric inlet of an ISPP process to selectively acquire CO<sub>2</sub> for use as a reactant gas, or within a process stream to separate CO<sub>2</sub> from other gaseous components.

The primary ISRU system that will benefit from the membrane technology is the Sabatier/Electrolysis (SE) process that reacts Martian atmosphere CO<sub>2</sub> with hydrogen to produce methane (fuel), water, and oxygen. These compounds will be extremely useful on Mars for use in rocket propellant and life support applications. The Martian



atmosphere is primarily CO<sub>2</sub>, providing an abundant and accessible resource for use as a reactant in the SE system. The atmosphere also contains a few percent nitrogen and argon, gases that could be separated and concentrated for use as inert gases for habitat inflation, pneumatic tools, and other pressurized gas applications. The CO<sub>2</sub> Acquisition Membrane (CAM) materials developed in this project will be used to purify the Mars atmospheric CO<sub>2</sub>, reducing interference from nitrogen and argon.

Specifically, this paper will include transport data for rubbery polymeric membranes including silicone rubber (poly(dimethyl siloxane or PDMS) and substituted polyphosphazenes tested at a range of pressure and temperature conditions.

## Experimental

### Membrane Materials

As shown in Figure 1 below, silicone rubber or poly(dimethyl siloxane) has an inorganic backbone composed of silicon and oxygen. Several square feet of a commercial PDMS composite membrane were generously donated by Membrane Technology and Research (MTR, Menlo Park, CA). This membrane has a 3.3 μm thick silicone rubber selective layer on a porous support fabric. According to MTR, the N<sub>2</sub> permeance (flux/ΔP) of this membrane at room temperature and pressure is 70 GPU's or  $7 \cdot 10^{-5} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}$ . The O<sub>2</sub>/N<sub>2</sub> ideal separation factor (permeance ratio) at room temperature and 1000 mbar feed pressure is 2.1.

Polyphosphazenes (PPZ) are inorganic polymers with a backbone consisting of phosphorus and nitrogen<sup>1</sup>. Properties can be

tailored by the choice of the organic pendant group attached to the P=N chain. These polymers have many desirable properties including excellent thermal stability and radiation resistance. PPZ samples used in this work were provided by the membrane group at the Idaho National Engineering and Environmental Laboratory (INEEL). Figure 1 below shows the structure of the PPZ polymer used in this work. Orme and coworkers<sup>1</sup> have shown that the CO<sub>2</sub> permeability of this polymer increases proportionally to the degree of 2-(2-methoxyethoxy)ethanol (MEE) substitution on the P=N backbone. Further, the glass transition temperature decreases as the degree of MEE substitution increases. For the 48% MEE substituted PPZ, the glass transition temperature is 230 K.

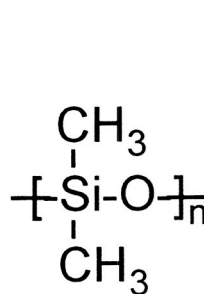


Figure 1. Chemical structure of the repeat unit for poly(dimethyl siloxane).

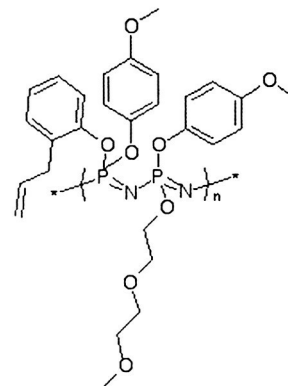


Figure 2. Substituted PPZ used in this work. Our samples have 48% 2-(2-methoxyethoxy)ethanol, 48% 4-methoxyphenol, and 2% 2-allylphenol as a cross-linking agent.

### Apparatus

A steady-state, continuous flow apparatus was used to measure gas permeance at the Colorado School of Mines. The design of this apparatus has been described previously<sup>2</sup>. Pure CO<sub>2</sub>, Ar, and N<sub>2</sub> used in

the permeance measurements were at least 99.995% purity and were used without further purification. As shown in Table 1 below, the Martian atmosphere contains approximately 95% CO<sub>2</sub>, 3% N<sub>2</sub> and 2% Ar. A standard mixture having this composition was used as the feed to the membrane cell in the mixture experiments.

A transient permeation apparatus was designed and built at Lockheed Martin for use in this project. The schematic diagram is shown in Figure 3 below. This apparatus has the capability to perform computer controlled measurements at sub-ambient pressure and temperature consistent with the Martian environment. A mass spectrometer is used to perform measurements with gas mixtures.

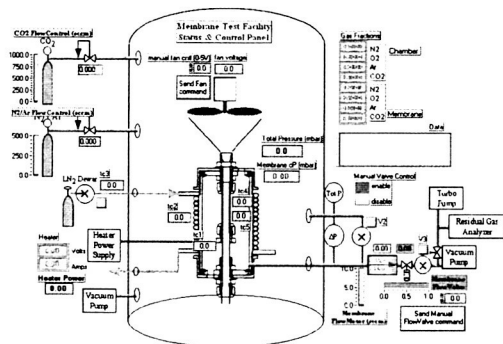


Figure 3. Membrane Test Facility (MTF) at Lockheed Martin.

The intent of the CAM experiments is to measure the gas separation capabilities of membranes on gas mixtures that simulate the Martian atmosphere. The pressure and composition of Mars atmospheric gases were measured by the Viking spacecraft, and are shown in Table 1. These data provide control loop set points for the chamber gas compositions used in CAM experiments.

## Theory

There are three primary performance parameters for membrane gas separation processes. The first is the permeability,  $P$ , which is the flux normalized by the driving force, or the gradient of the partial pressure of the gas of interest:

$$P_i = \frac{flux_i}{\Delta p_i} = \frac{flux_i \cdot thickness}{\Delta p_i} \quad (1)$$

Table 1. Martian Atmosphere Gas Composition and Temperature

| Parameter                    | Value       |
|------------------------------|-------------|
| Total Pressure               | 6 mbar      |
| CO <sub>2</sub> Gas Fraction | 0.95        |
| N <sub>2</sub> Gas Fraction  | 0.024       |
| Ar Gas Fraction              | 0.018       |
| Temperature Range            | 180 - 280 K |

The permeability is a materials property, and it is proportional to the product of the diffusivity and solubility of a penetrant. A closely related parameter is the permeance, or pressure normalized flux:

$$P_i/l = \frac{flux_i}{\Delta p_i} \quad (2)$$

The permeance is a property of the particular membrane of interest. Both permeability and permeance are productivity parameters. Finally, the degree to which the separation can be made is characterized by the selectivity or separation factor,  $\alpha$ , defined as the ratio of the permeabilities or permeances. The separation factor can be calculated using either pure gas permeabilities or those measured using gas mixtures. Due to a variety of factors (plasticization, competitive solubility, etc.), the ideal and mixed gas separation factors may not be the same<sup>3</sup>.

$$\alpha_{ij} = P_i / P_j \quad (3)$$

For transport of gases from binary mixtures, equation 4 below can be derived for the minimum permeate mole fraction of inert gases present in the permeate CO<sub>2</sub> stream from a membrane module used for ISPP

applications. This limiting case corresponds to zero CO<sub>2</sub> recovery and maximum purity. In equation 4 below,  $\alpha$  is the ideal separation factor, and  $x_o$  is the CO<sub>2</sub> mole fraction in the feed gas stream.

$$y_{p, \text{inerts}, \text{max}} = 1 - \frac{\alpha x_o}{\alpha x_o + (1 - x_o)} \quad (4)$$

Assuming the feed gas to the membrane process contains 95% CO<sub>2</sub>, equation 4 was plotted as a function of the ideal CO<sub>2</sub>/N<sub>2</sub> separation factor to estimate the minimum inert composition in the CO<sub>2</sub> permeate stream as a function of the ideal separation factor of the membrane material. This is shown in Figure 4.

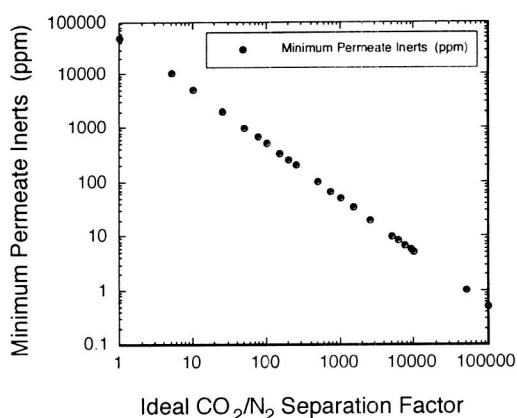


Figure 4. Effect of Ideal Separation Factor on the Minimum Inert Composition in the Permeate CO<sub>2</sub> Stream

## Results and Discussion

### Pure Gas Tests-PDMS

Pure gas permeation tests with CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> were performed at CSM with the MTR PDMS membrane over the temperature range 243 - 295 K at a differential pressure of approximately 0.55 Bar. Extrapolating our N<sub>2</sub> permeance data to 298 K using an exponential fit, we obtain an N<sub>2</sub> permeance of 62 GPUs from our measurements. This is within 10% of the value specified by MTR.

Our experimental O<sub>2</sub>/N<sub>2</sub> separation factor extrapolated to 25 °C is 1.94, within 8% of the MTR value.

The CO<sub>2</sub> permeation data and the CO<sub>2</sub>/N<sub>2</sub> ideal separation factor are plotted against temperature in Figure 5 below. A pure CO<sub>2</sub> permeance of 465 GPUs was measured using the CSM apparatus at 295 K, this agrees well (~3%) with a permeance of 450 GPUs measured at LM using the MTF at identical conditions.

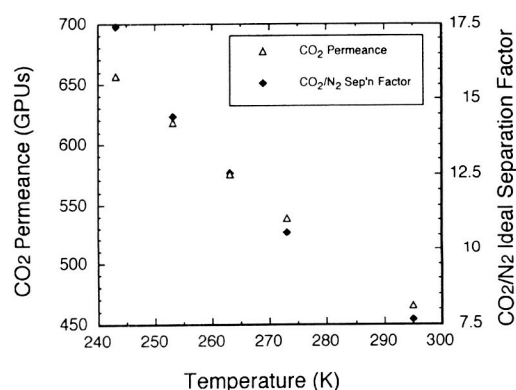


Figure 5. Effect of Temperature on the CO<sub>2</sub> Permeance and CO<sub>2</sub>/N<sub>2</sub> Permeance Ratio or Ideal Separation Factor for a  $\square P = 550$  mbar.

What is unusual about the data in Figure 5 is that both the CO<sub>2</sub> permeance and the separation factor increase as the temperature decreases. This suggests that the solubility of CO<sub>2</sub> in the silicone rubber membrane is increasing faster than the diffusivity is decreasing due to the decrease in temperature. For glassy polymers, a reduction in temperature often increases selectivity at a cost of a reduction in permeability<sup>3</sup>. Unfortunately, the combination of high permeance and moderate CO<sub>2</sub>/N<sub>2</sub> separation factor were not also observed during mixture measurements.

### Pure Gas Tests-PPZ

Table 2 presents preliminary permeability data for CO<sub>2</sub>, N<sub>2</sub>, and Ar for 135  $\mu$ m thick, composite membranes made from the 48% MEE substituted polyphosphazene polymer at 295 K. For a feed pressure of 80 mbar, the CO<sub>2</sub> permeability was 137 Barrer and the CO<sub>2</sub>/N<sub>2</sub> ideal separation factor was 48.5.

Table 2. Permeability Data for the 48% MEE Substituted Polyphosphazene at 295 K

| Feed Press,<br>mbar | Ideal Selectivity               |                     | Permeability (Barrer) |      |                 |
|---------------------|---------------------------------|---------------------|-----------------------|------|-----------------|
|                     | CO <sub>2</sub> /N <sub>2</sub> | CO <sub>2</sub> /Ar | N <sub>2</sub>        | Ar   | CO <sub>2</sub> |
| 800                 | 43.4                            | 17.6                | 2.86                  | 7.04 | 124             |
| 80                  | 48.5                            | 20.0                | 2.82                  | 6.82 | 137             |

The permeabilities we measured for CO<sub>2</sub> at 295 K with feed pressures less than 800 mbar are up to 18% higher than those reported for the same PPZ polymer measured at 303 K with a higher feed gas pressure of 2900 mbar<sup>1</sup>. This may be due to a Langmuir type sorption isotherm for CO<sub>2</sub> in PPZ. We expect that higher degrees of MEE substitution in the PPZ polymer should further increase the CO<sub>2</sub> permeability measured at low pressure and temperature conditions.

#### Mixed Gas Tests-PDMS

Permeation tests with the MTR PDMS membrane using a feed mixture simulating the Martian atmosphere (95% CO<sub>2</sub>, 3% N<sub>2</sub>, and 2% Ar) were performed at CSM. These data are plotted in Figure 6 as a function of temperature with CO<sub>2</sub> partial pressure driving force as a parameter. These tests were intended to be screening tests prior to experiments at LM under actual Martian atmospheric conditions.

In order to try to simulate partial pressure driving forces less than normal atmospheric pressure in Golden, CO of approximately 800 mbar, the CSM apparatus was operated

using several different operating modes. The lowest CO<sub>2</sub> partial pressure difference of 355 mbar was achieved by diluting the feed mixture with He and using a He sweep gas on the permeate (product) side of the membrane. The intermediate CO<sub>2</sub> partial pressure driving force of 573 mbar was achieved using the Martian atmospheric gas mixture as the feed to the membrane cell and a He sweep gas. Finally, the highest CO<sub>2</sub> partial pressure driving force was achieved by using the Martian atmospheric mixture as the feed gas and no sweep gas. The permeate gas stream had a large enough flow rate to simply flow to the gas sampling valve on the gas chromatograph.

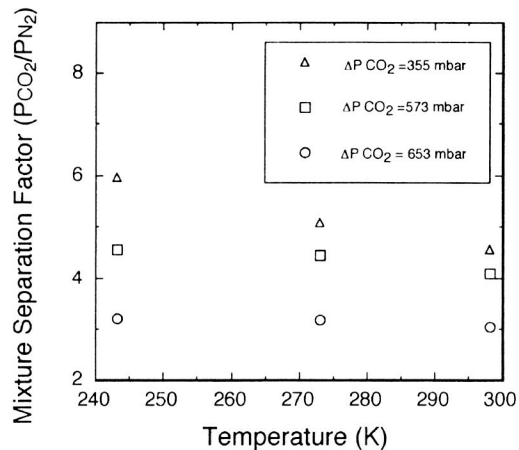


Figure 6. Effect of Temperature on the CO<sub>2</sub> Permeance and CO<sub>2</sub>/N<sub>2</sub> Permeance Ratio or Mixture Separation Factor.

The separation factors measured for the mixture tests were up to a factor of three lower than those observed for the pure gas permeation tests. In general, the lower the CO<sub>2</sub> partial pressure difference, the larger the separation factors. The mixture separation factors ranged from 4.5 to 6 for the lowest CO<sub>2</sub> driving force as the temperature increased from 243 to 298 K. For the highest CO<sub>2</sub> driving force of 653 mbar, the separation factors increased from 3 to 3.2 over the same temperature range.

The effect of temperature in the mixture permeation tests was that the separation factor increased as the temperature decreased. This effect was qualitatively similar to that seen in the pure gas tests.

The primary reason for the decline in the mixture separation factors for the PDMS membrane can be seen in Figure 7, a plot of CO<sub>2</sub> and N<sub>2</sub> mixed gas permeances measured at CSM. At a constant temperature of 243 K, the CO<sub>2</sub> mixed gas permeance is approximately constant at 155 GPUs until the partial pressure driving force decreases to below 200 mbar. This average CO<sub>2</sub> permeance is significantly lower than the value of 650 GPUs measured for pure CO<sub>2</sub> at 243 K and 550 mbar shown in Figure 5 above. However, the N<sub>2</sub> permeance measured at 243 K and 550 mbar partial pressure difference was 37 GPUs, in reasonable agreement with the range of N<sub>2</sub> permeances in Figure 8 measured at low partial pressure differences. Therefore, the CO<sub>2</sub> mixed gas permeances were about a factor of four lower than the pure gas values. The possible reasons for this difference could be depression of CO<sub>2</sub> solubility in the membrane due to the presence of N<sub>2</sub> and Ar or structural changes in the PDMS polymer at low temperatures. The glass transition temperature for PDMS is ranges from 233 to 243 K<sup>4,5</sup>, very close to our lowest experimental temperature. A change from a rubbery state to a glassy state would greatly reduce the CO<sub>2</sub> permeability, which is consistent with the mixed gas permeation data.

#### Module Design Calculation

Using the algorithms described by Shindo et al.<sup>6</sup>, a Mathematica function was written to perform membrane module design calculations for candidate ISRU systems at

actual scale that may one day operate on the surface of Mars. A preliminary calculation of membrane module area needed to supply 2.5 liters/minute of CO<sub>2</sub> to the ISPP process was performed as a function of feed pressure assuming the feed gas composition was 95% CO<sub>2</sub> and 5% N<sub>2</sub>. The CO<sub>2</sub> permeate flow rate basis of 2.5 L/min was chosen as that required to produce a CO<sub>2</sub> reactant stream for production of methane using the Sabatier Electrolysis process. The permeate pressure was assumed to be 10<sup>-3</sup> mBar.

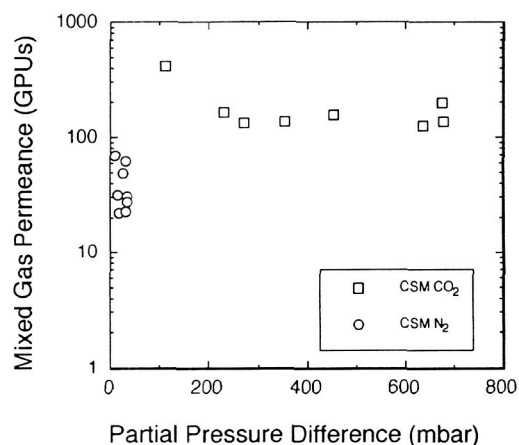


Figure 7. Effect of partial pressure driving force on the CO<sub>2</sub> and N<sub>2</sub> mixed gas permeances at 243 K

Two cases were run, one corresponding to a high CO<sub>2</sub> permeance of 650 GPUs and a moderate CO<sub>2</sub>/N<sub>2</sub> selectivity of 17. The other case corresponds to a lower CO<sub>2</sub> permeance of 34 GPUs and a higher CO<sub>2</sub>/N<sub>2</sub> selectivity of 50.

A series of design calculations were done by varying the feed pressure to the membrane module that ranges from 10 mBar to 120 mBar. As Figure 8 clearly shows, the required membrane area is very sensitive to the feed pressure, and drops from 108 ft<sup>2</sup> to approximately 10 ft<sup>2</sup> as the feed pressure increases for the high permeability case. A scroll pump could be used to increase the

feed pressure substantially using very little power (several Watts). Assuming a spiral wound module area/volume ratio of  $300 \text{ ft}^2/\text{ft}^3$ ,  $10 \text{ ft}^2$  of membrane area would have a volume of only  $0.035 \text{ cubic ft}$ .

For the lower permeability case, we assumed that a 4 micron thick, commercial membrane could be fabricated from the polyphosphazene or similar rubbery polymer. Given that the  $\text{CO}_2$  permeability for the PPZ polymer is about a factor of 19 lower than PDMS, the required membrane area is considerably higher. However, about  $300 \text{ ft}^2$  are required for a feed pressure of 100 mbar. Given that a well-designed spiral wound module can have a surface area to volume ratio of  $300 \text{ ft}^2/\text{ft}^3$ , this module would required about  $1 \text{ ft}^3$  for the membrane module.

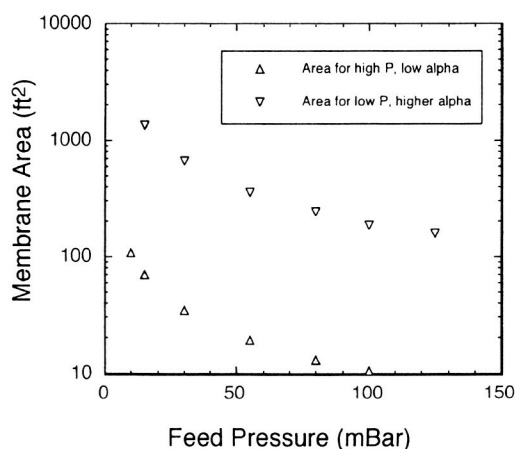


Figure 8. Effect of feed pressure on membrane area required to produce  $2.5 \text{ L/min CO}_2$ . One set of calculations was done for a  $\text{CO}_2$  permeance of 650 GPU and  $\alpha = 17$ , the other case has a  $\text{CO}_2$  permeance of 34 GPU and an  $\alpha = 50$ .

## conclusions

The concept of using synthetic membranes for the separation and purification of carbon dioxide ( $\text{CO}_2$ ) from the Martian atmosphere for *In-Situ Resource Utilization (ISRU)* is introduced. Pure gas and mixed gas

permeation tests with  $\text{CO}_2$ , Ar,  $\text{N}_2$ , and  $\text{O}_2$  were performed over the temperature range 243 K to 295 K with a several candidate membrane materials including rubbery polymers (silicone rubber and substituted polyphosphazenes).

In experiments with commercially available silicone rubber membranes, the pure gas  $\text{CO}_2$  permeance (flux/driving force) increases from 460 GPU to 655 GPU as the temperature decreases from 295 K to 243 K. The ideal carbon dioxide/nitrogen separation factor (ratio of pure gas permeances) increases from 7.5 to 17.5 over the same temperature range. However, in mixed gas experiments, the  $\text{CO}_2/\text{N}_2$  separation factor was much lower, increasing from 4.5 to 6 as the temperature decreased from 295 K to 243 K for a  $\text{CO}_2$  partial pressure difference of 355 mbar.

Preliminary permeability data for  $\text{CO}_2$ ,  $\text{N}_2$ , and Ar for a 48% MEE substituted polyphosphazene polymer were measured at 295 K. For a feed pressure of 80 mbar, the  $\text{CO}_2$  permeability was 137 Barrer and the  $\text{CO}_2/\text{N}_2$  ideal separation factor was 48.5.

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## References

1. Orme, C. J., Harrup, M. K., Luther, T. A., Lash, R. P., Houston, K. S., Weinkauf, D. H., and F. F. Stewart, "Characterization of Gas Transport in Selected Rubberty Amorphous Polyphosphazene Membranes," *J. Membr. Sci.*, **186**, 249-256(2001).
2. Bateman, B.R., Way, J. D., and K.M. Larson, "An Apparatus for the Measurement of Fluxes through Immobilized Liquid Membranes," *Sep. Sci. & Technol.*, **19**, 21-32 (1984).
3. Mulder, M., "*Basic Principles of Membrane Technology*," Kluwer Academic Publishers, Boston, 1996.
4. Molnar, L. and A. Huba, "Measurement of Dynamic Properties of Silicone Rubbers," *Periodica Polytechnica Ser. Mech. Eng.*, **45**, 87-94(2001)
5. Robb, W. L., "Thin silicone membranes- Their permeation properties and some applications," *Annals New York Academy of Sciences*, **146**, 119(1968).
6. Shindo, Y., Hakuta, T, and H. Yoshitome, "Calculation Methods for Multicomponent Gas Separation by Permeation," *Sep. Sci & Technol.*, **20**, 445-459(1985).